European
Environmental Research Group Inc.
MiljøForskerGruppen ApS.

**Kemisk-Tekniska Leverantörförbundet**

**Stockholm**

# Polyphosphate, Zeolite and Citrate in Detergents

## Technical and Environmental Aspects of Detergent Builder Systems

**Final Report**
**December 1996**

European
Environmental Research Group Inc.
MiljøForskerGruppen ApS.

**Kemisk-Tekniska Leverantörförbundet**

**Stockholm**

# Polyphosphate, Zeolite A and Citrate in Detergents

## Technical and Environmental Aspects of Detergent Builder Systems

**Final Report**

**December 1996**

| | | |
|---|---|---|
| Document No. | : | 95002 |
| Edition No. | : | 06 |
| Date | : | 25/10/01 |
| Written by | : | Jens Folke |
| Quality control | : | KTF |

European Environmental Research Group

16, Østergade
3250 Gilleleje
Denmark
Tel. +45 4835 4541
Fax +45 4835 4542

12, Teknikvägen
SF-021150 Esbo
Finland
Tel. +3580 4354 2076
Fax +3580 4554 403

35, Götgatan
S-116 21 Stockholm
Sweden
Tel. & fax:
+46 8 643 37 59

Fryksta
S-665 00 Kil
Sweden
Tel. +46 554 405 50
Fax +46 554 405 59

The correct citation of this report is:

Folke, J., 1996. “Phosphate, Zeolite and Citrate in Detergents—Technical and Environmental Aspects of Detergent Builder Systems”. Report No. 95002/06, written by *MFG—Environmental Research Group*, Gilleleje, Denmark, for *Kemisk Tekniska Leverantörförbundet*, Stockholm.

# Table of Contents

# Preface

Internationally as well as in the Nordic countries great attention has been focused on the role of phosphorus in eutrophication and deterioration of the water quality of our receiving waters. This has led to a ban of phosphate containing detergents in some countries, e.g. Switzerland and Norway, and to limitations in its use in many other countries. The detergent industry was forced to develop new builder systems, and as zeolite had already been on the market for other purposes, Zeolite A was early identified as a potential substitute for phosphate. Later, the compact liquid detergents based on citrate/fatty acids also got a significant market share.

Many efforts have been carried out by the detergent industry to develop new, phosphate-free detergents, and today it is generally felt that the new formulations are equally as good as the phosphate-based ones. The phosphate producers have not been satisfied with this development as they felt that it was unjustified to ban the use of phosphates in all those instances where secondary + tertiary treatment of the municipal sewage was applied prior to discharge. Therefore, the phosphate industry, and in Europe the CEEP (Centre Européen d'Etudes de Polyphosphates) and SCOPE (Scientific Committee on Phosphates in Europe) have sponsored a vast amount of studies and used large resources on information campaigns to try to get a more balanced message across than the message conveyed by the environmental authorities in those countries that were banning STPP based detergents. And quite rightfully, efficient wastewater treatment of municipal sewage prior to discharge using secondary + tertiary treatment will remove phosphates from the effluent to a level that is independent on the use of phosphate based detergents. Many of the above mentioned studies have come to the conclusion that the phosphate built products are generally superior to the other detergent products. However, in many cases, these results may be a reflection of the experimental design, rather that an outcome of objective comparisons. This has confused the discussion, and the detergent industry represented by the companies stated below has felt a growing need to try to balance some of the views expressed in these studies.

Therefore, the detergent industry has approached the Swedish Cosmetic, Toiletry and Household Products Suppliers Association (KTF), which has commissioned the European

Environmental Research Group in Denmark (MFG-DK) to evaluate pertinent literature on detergent builders. MFG-DK is an independent research and consulting company, which is part of the "European Environmental Research Group" consortium, having sections in Sweden, Finland and Denmark.

It is the hope of our industry that the report will be helpful for people involved with consumer protection and environmentally compatible products, e.g. green labelling and green choices. The report deals exclusively with the aspects of textile detergent builder systems, particularly phosphorus and the most common builders used to substitute phosphorus or phosphorus/polycarboxylate, i.e. zeolite A /polycarboxylate and citrate/fatty acid.

Stockholm 1996.

The Swedish Cosmetic, Toiletry and Household Products Suppliers Association (KTF)

Christina Mattsson, Director.

# Acknowledgements

This report has been written as contract work for The Swedish Cosmetic, Toiletry and Household Products Suppliers Association (KTF) by Jens Folke from the European Environmental Research Group in Denmark (MFG-DK). Christina Olivecrona, who is an independent consultant, reported a preliminary, but very useful literature study to Procter & Gamble Scand. Inc. To supervise the project, KTF established a steering committee consisting of Mats Hagwall, KTF, Lotta Nilsson, Colgate-Palmolive AB, Anders Nordström, Hackman Havi OY AB, Mats Landén, Lever AB and Maria Pettersson, Procter & Gamble Scand. Inc. I want to thank the members of this committee for the time and effort spent on this project.

The draft report has been reviewed by professional people in the organisations of the four companies. I want to thank them for providing critique as well as many valuable comments. The draft report was also reviewed by staff at ZeoDet, Henkel and Kemira. I also want to thank the representatives of these companies for their time and effort to secure that all aspects of the sunject were considered.

I apologise, if some people feel that their comments have not been taken fully into account. The comments received from all the different experts were not always consistent, but it is well-known that even the experts do not always agree on all details. I have had to make the necessary professional judgements on conflicting comments received and the quality of data available. It has been our aim to check that all conclusions in the report are supported by reliable data and defensible to the extent feasible within the budgetary restraints. It should, however, be pointed out that solely the author is responsible for the contents and the conclusions of this report.

Gilleleje, November 1996.

Jens Folke
MFG-DK.

# 0. Summary


The Swedish Cosmetic, Toiletry and Household Products Suppliers Association (KTF) has commissioned the European Environmental Research Group to evaluate literature on detergent builders, i.e. sodium tripolyphosphate, Zeolite A /polycarboxylate and sodium citrate/fatty acid as builder systems. As stated in the Preface, the objective was to create a balanced review of current knowledge within the field of laundry detergent builders.

Raw materials

Phosphate is produced from phosphate rock. On a world-wide basis, there is an ample supply of phosphate rock for the foreseeable future. However, some countries have reserves for hundreds of years, whereas other countries have resources that are much more limited. Approximately 95% of the world's economic phosphate reserves are held by the world's present top 10 producing countries [van Kauwenberg, 1992]. Raw materials for zeolite manufacturing are even more plentiful than phosphate rock reserves. Raw material for citrate is biomass, which is essentially a renewable resource.

Builder systems

Sodium tripolyphosphate (STPP) is a detergent builder with a variety of positive, proven effects on the washing process [Gleisberg, 1992]. No single substitute detergent builder combines all these properties, but may have additional unique properties. "Phosphate-free" products, e.g. those using zeolite or sodium citrate, require that the rest of the formulation is modified in order to maintain similar good performances and properties. Co-builders such as polycarboxylate or fatty acids may have to be used.

Surfactants

The content of surfactants in detergents using different builder systems is roughly the same in the case of non-ionic surfactants, but varies greatly when it comes to anionic surfactants. The relative amount of anionic surfactants in zeolite and phosphate detergent systems is of roughly similar size. In liquid detergents, where the builder system is made of fatty acids/ citrate, larger amounts of anionic surfactants are used. In phosphate based as well as in some zeolite based detergents, sodium sulphate is added to improve the solubility and efficiency of surfactants.

Dosage and effects

There are several low-dosage phosphate and zeolite based detergents available and also among the high dosage detergents, there are both phosphate and zeolite based ones.

The fatty acids/citrate builders are mainly used for compact liquid detergents. If dosed correctly, the lowest consumption of surfactant per wash is obtainable when using modern STPP based detergents, although this may vary from brand to brand. The most recent zeolite based detergents are also low in the amount of surfactant used per wash. Apparently, it is very important to use the correct dosage of zeolite based detergents. Incorrect dosage and usage (of any kind) of a detergent can lead to problems with encrustation. Based on the information given at a seminar at KTF in February 1996, on the functionality of laundry detergents, there is no support for the suspicion that phosphate-free detergents cause more wear and tear than STPP based detergents on washing machines. At least, this has not been the case according to the statistics on machine repairs presented by several manufacturers at the seminar. Many problems arise because of cold water washing. Generally, it is recommendable to wash at temperatures between 40°C - 60°C.

Sewage treatment systems

Irrespective of the builder system used, effluents from the washing of laundry using modern detergents must pass an advanced biological wastewater treatment facility to become environmentally compatible. However, there have been speculations regarding the role of fatty acids and surfactants in causing the recent problems of foaming and less efficient oxygen transfer in aerators. These problems need to be studied in more detail. As this is not directly linked to the choice of builder systems, the subject is only briefly touched on in this report.

The amount of phosphorus in the raw sewage influences the total cost of sewage treatment. However, the concentration in the final effluent is determined by the choice of treatment process, rather than by the concentration of phosphorus in the influent. Biological phosphorus removal can be used down to a level of 1.0 – 1.5 mg/L[1], while lower levels require the use of chemical coagulants such as alum or ferrochloride. Sometimes higher phosphate loads can be treated in these systems without additional cost once the capital expenditure for building the biological phosphorus removal plant has been depreciated.

Compared to STPP-based detergents, zeolite-based detergents increase the sludge load additionally by 10 – 15% based on dry

[1] Biological excess phosphate removal plants regularly do better than this in South Africa and Germany. Further, moderately higher phosphate loads can be treated without additional cost once the capital expenditure for building the plant has been depreciated. Few plants in Scandinavia are currently built this way.

weight, unless large amounts of coagulants are used to precipitate phosphorus—the cause being the inert zeolite and a lower sludge index[2]. Thus, the effluent quality should thus be better with regard to suspended matter and soluble COD, but the treatment costs for sludge handling will increase.

The use of citrate based builders results in an additional BOD-load, but this is a minor cost factor overall compared to the costs of sludge handling. Although the cost differences in sewage treatment between the three builder systems are significant, they are not easily quantified at a general level. It is more expensive to handle an increased sludge load than an increased BOD load. Therefore, sewage treatment of the effluents from washing of laundry with STPP based detergents is more expensive than treatment of effluents from the washing of laundry with zeolite based detergents. These, in turn, are more expensive than treatment of effluents from the washing of laundry with citrate based detergents.

Effluent discharge

If laundry washing effluents are discharged with untreated wastewater the zeolite/polycarboxylate based detergents are probably the better choice of the three, due to the higher content of inert material—but all detergents present a problem in this case. There are situations when some sewage treatment works have a reduced capacity, e.g. during prolonged periods of hard frost or during days with heavy rainfalls. In situations where this leads to discharge of untreated sewage, STPP based detergents must be regarded as the least environmentally compatible ones, due to the larger effect on eutrophication (i.e. stimulation of algal growth) caused by phosphorus than by BOD. Also, modern surfactants although biodegradable, are known to be ecotoxic to aquatic organisms ($EC_{50} \approx 1$ mg/L), and such discharges are unwanted in all cases. If secondary but not tertiary treatment is used, zeolite or citrate based detergents are also preferential to STPP based detergents, because the larger P-load from STPP based detergents can only be handled in tertiary treatment or biological phosphorus removal.

Sludge handling

If P-removal is applied, by far the largest fraction of phosphates are removed with the sludge. STPP based detergents are only preferential to the two other builder systems, if coagulants are used appropriately (i.e. not overdosing the coagulant as this increases the amount of sludge, and the precipitated phosphate has a lower bioavailability than biologically bound phosphate) and the biosludge is spread on agricultural land. Then STPP has an

[2] The sludge index is a measure of the ability of sludge to settle.

advantage compared to the other builder systems in that the sludge has a better fertilizer value. Spreading of the sludge on agricultural land is the environmentally best choice in cases where heavy metals and other xenobiotic compounds are not too high in concentrations.

Health

From a health perspective the here discussed builder systems are all safe in use. In some cases, zeolite-based detergents have been shown to leave more residues in cloth, and dermatologists have seen this as a possible source of skin irritation. However, at this point tests with Zeolite A revealed no evidence for this hypothesis.

Life cycle considerations

The life-cycle assessments (LCA) of detergent builders are indeed very complicated, and there are so many local factors involved that LCA, so far, has not provided a universal answer as to which builder system is the environmentally most compatible one. Factors, such as hardness of water, actual sewage treatment, laundry habits etc., are so variable that any detergent builder system will turn out to be the preferable one under a specific set of circumstances. The first LCA study of a builder, conducted according to the ISO Guidelines (SETAC) addresses zeolites only [Hauthal, 1996]. The ISO Guidelines were not issued, when SCOPE funded the so-called "Landbank" LCA studies were conducted [Wilson & Jones, 1994; Wilson & Jones, 1995]. Therefore, an in-depth LCA study on the STPP builder conducted in accordance with the ISO Guidelines is needed in order to compare zeolites and phosphates appropriately.

# 1. Introduction

The Swedish Cosmetic, Toiletry and Household Products Suppliers Association (KTF) has commissioned the European Environmental Research Group to evaluate literature on detergent builders, i.e. sodium tripolyphosphate (STPP), Zeolite A/P, polycarboxylate (PCA) and sodium citrate/fatty acid as builder systems with respect to:

1. Technical aspects.
    a. Manufacturing.
    b. Washing efficiency.
    c. Effects on sewage treatment plants.
2. Health aspects.
3. Environmental aspects.
    a. Receiving water
    b. Sludge from municipal treatment plants.
4. Life cycle analysis (LCA) considerations.

A steering committee headed by Mats Hagwall, KTF, assisted me in collecting data, commenting on drafts etc. This committee also organized a workshop on washing efficiency in Stockholm to assist me in closing gaps in the open literature.

The background of the study is briefly explained in the Preface.

# 2. Technical aspects

STPP is a detergent builder with a variety of positive properties for the washing process:

- Complexes with metal ions that give the water hardness. This prevents encrustation in the fabrics and washing machines and precipitation of surfactants.
- Provides alkalinity and buffer-capacity to stabilize pH.
- Assists deflocculation of dirt and particles.
- Increases the electrolytic activity of the wash water, thereby loosening chemical-physical bonds between dirt and substrate.
- Is mixable with other components in the product and improves the physical characteristics of detergent powders.
- Is non-toxic to the consumer.
- Can be used in both liquid and granular products.

No single substitute detergent builder has all these properties, so “phosphate-free” products, e.g. using Zeolite A, require that the rest of the formulation is modified in order to maintain good performance and properties. In particular, sodium citrate, polycarboxylate[3] (PCA), and sodium carbonate are needed as co-builders in zeolite based detergents [Christophliemk et al., 1992]. Much less or even zero polycarboxylate can be used in case of a new, improved zeolite quality, Zeolite P [Upadek et al., 1996], which has already started to be used in some detergents. However, Zeolite A is still dominating the zeolite market.

Typical formulations

Typical new formulations of three groups of detergents are presented in Table 1. Defining the term *typical* is difficult, and it means that no product exactly matches the speficiations. The variation in the content of surfactants in detergents using different builder systems is very great. One could have used non-compact formulations, e.g. for Zeolite A, as was suggested by Kemira [1996]. However, I have chosen to present data on compact, new fomulations in order to reflect the current market situation in Scandinavia.

[3] PCA need not be used in STPP based formulation, if the STPP content is high enough, but many phosphorus based compact detergents contain up to 3% PCA [ZeoDet, 1996].

**Table 1. Typical formulations of new compact citrate/fatty acid, Zeolite A/PCA and phosphate based detergents.**

| | Colour Liquid Fatty acid | Compact Powder Zeolite A | Compact Powder Phosphate |
|---|---|---|---|
| **Surfactant system** | | | |
| Anionic, e.g. LAS | 5-25% | 10-15% | 0-15% |
| Nonionic, e.g. alkylethoxylates | 10-25% | 5-10% | 10-15% |
| **Builder system** | | | |
| Fatty acid (palm kernel, rape seed) | 7-10% | | |
| Zeolite | | 15-25% | |
| Silicate | | 2-12% | 3-6% |
| STPP | | | 30-50%[Å] |
| Citric acid | 3-5% | 0-5% | 0-5% |
| Carbonate/bicarbonate | | 5-10% | 5-10% |
| **Solvents** | | | |
| Propylen glykol + ethanol + glycerol | 10-15% | | |
| **Bleach system** | | | |
| Percarbonate | | 20-25% | |
| Sodium perborate | | or 10-15% | 10-15% |
| Phosphonate | | <0.2% | <0.2% |
| TAED | | 3-5% | 3-6% |
| **Polymers** | | | |
| Silicone | <1% | <1% | <1% |
| Polyvinylpyridinoxide | | +[Ñ] | +[Ñ] |
| Polycarboxylate | | 3-6%[Ç] | 0-3%[É] |
| CMC | | +[Ñ] | +[Ñ] |
| **Other** | | | |
| Enzymes, phosphonate, perfume | <1-2% | <1-2% | <1-2% |
| Sodium sulphate | | 2-6% | 0-5% |
| **Water** | | | |
| Hydrate water | | 5-10% | 10-15% |
| Free water (balance) | 40% | <1% | <1% |
| **Dosage** (0 - 6° dH, low/normally soiled) / 3.5 kg laundry | 50 ml | 40 g | 50 g |

[Å]Scandinavia is in the lower end of this range compared to the rest of Europe.
[Ç]In case of Zeolite P, PCA is not needed.
[É]E.g. Via TAED 6040 in Sweden or Colon Total / Camp in Spain contains 3% PCA.
[Ñ]In some brands.
Source: [Procter & Gamble; Colgate-Palmolive; ZeoDet].

In liquid detergents the builder system is made of fatty acids/citrate and larger amounts of anionic surfactants are used. In regular (non-compact) phosphate and zeolite based detergents, sodium sulphate is added to improve the solubility and efficiency of surfactants.

## 2.1. STPP

Manufacturing

The raw materials for STPP are either black phosphate rock or apatite. Both phosphorus sources are much in demand for use in fertilizers. More than 30 countries are presently processing phosphate rock, but approximately 95% of the world's economic phosphate reserves are held by the world's present top ten producers. Phosphoric acid can be produced by a number of processes—a commonly used one involves treatment of the rock with sulphuric acid and subsequent purification, before treatment with soda ash (sodium carbonate) to produce "ortho liquor". STPP is formed after spray drying and calcination in a large revolving kiln, in which water is eliminated to form STPP with the following formula:

$$Na_5P_3O_{10}$$

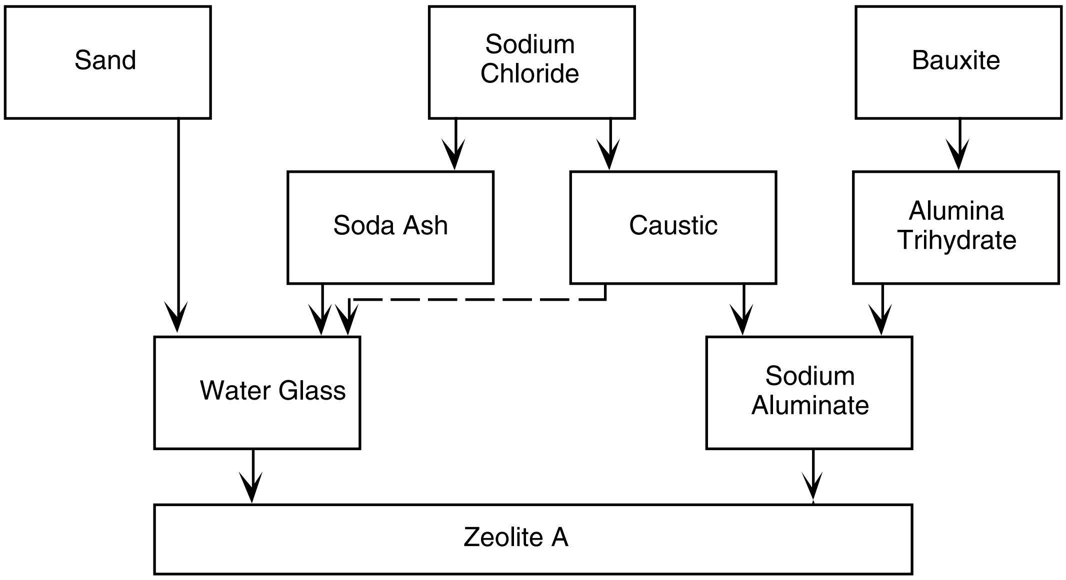
The content of heavy metals, including cadmium, varies a lot depending on the source. Apatite is very low in heavy metals, while black phosphate rock can contain quite high levels. If present, heavy metals are mostly isolated in a solid waste fraction of calcium sulphate. Before 1992, approximately 90% of the world production of phosphate rock was consumed by the fertilizer industry. The remaining 10% are used for the manufacturing of animal feed, detergents and other chemicals [Gregory, 1992]. Updated information on this issue is available from the International Fertilizer Manufacturers' Association (Rue Marbeuf 9, Paris).

Environmental pollution

The main environmental burden associated with STPP manufacturing is the phosphogypsum discharge including certain heavy metals as well as the energy required in the process. Actual figures depend on the source of raw material, and the individual production process. Figures from Britain show that ≈60 $m^3$/tonne STPP of wastewater and ≈130 $m^3$/tonne STPP of cooling water are used[4]. The phosphogypsum waste contains 2 – 13 mg Cd/kg, but this obviously varies with the source of raw material. In some countries, the gypsum is discharged at sea or deposited in landfills. In some cases it is possible to reuse it in saleable products [Wilson & Jones, 1994].

The only place in the Nordic countries where deposition of phospho-gypsum occurs is in Finland. Finnish apatite is very

[4] Apparently a miscalculation is presented in the source, so the correct figure should be ≈20 $m^3$/tonne STPP of wastewater and ≈170 $m^3$/tonne STPP of cooling water [Kemira, 1996].




Source: [Christophliemk et al., 1992]

*Figure 1. Manufacturing of Zeolite A*

low in cadmium, and some of the gypsum is reused for various purposes [Kemira, 1996].

## 2.2. Zeolite A

Manufacturing

Sodium zeolite A is the principal alternative to phosphate as a detergent builder, serving to soften the washing water mainly by calcium ion exchange. It has the following formula:

$$Na_{12}(AlO_2)_{12}(SiO_2)_{12} \cdot 27H_2O$$

It is mainly manufactured through two distinct routes:

- Calcination of clays such as kaolin or montmorillonite in a concentrated sodium hydroxide solution.
- Reacting sodium silicate with sodium aluminate in an alkaline solution.
- Spray drying can be used as the final treatment in both processes.

The caustic comes from the chlor-alkali process, where chlorine is used elsewhere (e.g. for water disinfection and PVC production).

Environmental impact

The conversion of bauxite to alumina trihydrate creates a waste material known as “red mud” in an amount of 1-2 tonnes (fresh weight)/tonne product [Ullmann, 4th ed.]. In the past, this mud was frequently discharged to the marine environment, but today the mud is drained and deposited inland [Ullmann, 4th ed.]. This mud contains phosphate and trace amounts of mercury [Wilson & Jones, 1994]. Zeolite A is basically produced from alumina trihydrate without any further waste materials [Christophliemk et al., 1992]. Wastewater in an amount of ≈7 $m^3$/tonne (or less) zeolite is produced and ≈44 $m^3$/tonne zeolite of cooling water is used. The main environmental impact associated with zeolite manufacturing is related to generation of the energy required to produce e.g. sodium hydroxide from brine. The supply of the raw materials for zeolite: sand, sodium chloride, bauxite or kaolin is plentiful [Wilson & Jones, 1994].

EAWAG, the independent Swiss research institute, has concluded that both Zeolite A and Zeolite P are environmentally acceptable builders [Alder et al., 1996].

## 2.3. Citrate

Manufacturing

Citrate in combination with free fatty acids is another builder system that has been used to substitute STPP. The chemical formula is:

$$\begin{array}{c} CH_2COOH \\ | \\ HO\text{–}C\text{–}COOH \\ | \\ CH_2COOH \end{array}$$

It is currently produced by microbial fermentation, from 1970 by a yeast culture of the *Candida* genus, e.g. *C. lipolytica* or *C. guilliermondi* [Kirk-Othmer, 1985] from substrates of molasses or $C_9$ to $C_{20}$ normal paraffins [Hoyt & Gewanter, 1992]. In modern processes an energy requirement of 1.3 – 2.6 MJ/$m^3$ of fermenting medium is sufficient for both cooling and aeration. A citrate concentration of up to 100 mg/L has been achieved. Citric acid is generally recovered from the fermented aqueous solution by first separating the micro-organisms and then precipitating the citrate ions as the insoluble calcium salt or by a solvent extraction process. Purification is achieved by acidification, filtration/distillation of insoluble/volatile impurities to produce a concentrated citric acid solution (≈50%). Further clean-up in activated charcoal columns is sometimes carried out, and crystalline citric acid can also be produced. The residual solubles and biomass from the fermentation can be recovered and used as animals feeds.

Environmental impact

Today, China is the dominant producer of citric acid, as Chinese producers have been able to market citric acid at prices lower than OECD producers have been able to meet. The environmental performance standard of the Chinese facilities is unknown to me. Therefore, it is not possible to report thermodynamical data to compare to Zeolite A and STPP. The environmental fate of the residual biomass from fermentation is a key issue in the environmental evaluation of citrate as a detergent builder.

## 2.4. PCA

In connection with detergents, the term "polycarboxylates" is frequently used to designate water-soluble linear polymers of acrylic acid ($CH_2$=CHCOOH):

Homopolymer of acrylic acid (P(AA)):
—$[CH(COONa)–CH_2]_m$—

or a mix of acrylic and maleic acids:

Copolymer of acrylic and maleic acids (P(AA-MA))
—$[CH(COONa)–CH_2]_m$—$[CH(COONa)–CH(COONa)]_n$—

The term "polyacrylate" is normally avoided in favour of polycarboxylates (PCA) as polyacrylates used elsewhere include esters of the acrylic acid. PCA have been used since the early 1980s, in low-phosphate and phosphate-free detergents. Their effect is based on the dispersion of calcium carbonate or of calcium phosphate and the soil detached during washing [Opgenorth, 1992]. Between 2 and 5 % of PCA were used in phosphate-free detergents based on zeolite/sodium carbonate, but recently, new formulations and development of new zeolites have reduced the amounts added. For example, Lever now has a formulation based on a new Zeolite P, which does not contain any PCA at all [Crosfield, 1996].

Manufacturing

Polycarboxylates are produced industrially by free radical polymerization of the monomeric acrylic acid alone or in a mixture with maleic acid to produce P(AA) and P(AA-MA). The mean molecular mass of PCA used for detergents is generally between 1000 and 100,000 amu. The amounts used have increased during the past 15 years, e.g. in Germany the amount used was 15,000 tonnes in 1987 and 19,000 tonnes in 1990 when the marketshare for phosphate-free detergents was over 95% [Opgenorth, 1992]. Probably, the Scandinavian situation is quite similar to the German one, i.e. an estimate of 6,000 tonnes of PCA were used in Sweden in 1990. The amounts of PCA used in Scandinavia have probably peaked due to new detergent formulations using less PCA, and recently due to ecolabels, e.g. the Nordic Swan, now allowing also phosphate detergents to be ecolabelled.

Environmental impact

Manufacturers and users of PCA have carried out extensive investigations on the environmental compatibility of PCA [Opgenorth, 1992; ECETOC, 1993]. PCA is sparingly soluble in water when calcium ions are present in concentrations above 1.43 mmol/L and the polymer concentration is between 100 and 500 mg/L. At a PCA concentration of 1000 mg/L, however, this type of precipitation does not occur, since calcium is no longer present in excess, and this is used during washing. In the sewer, the PCA concentration goes down while the calcium concentration normally remains higher than 1.43 mmol/L. Therefore, PCA precipitates and is eliminated with other solids from the sewage, provided the coagulation is a result of water hardness. The tendency to form insoluble calcium PCA increases with the charge density and the molecular mass of the polymers [Opgenorth, 1992].

Normally, the coagulation of PCA is a slow process. P(AA-MA) 70,000 was found to precipitate > 80% in 4 days. This points towards secondary clarification being the most important route for the elimination of PCA from the treated effluent, unless the residence time in the sewer is a matter of days. If so, mechanical treatment will also eliminate PCA. PCA have not been found to interfere with the operation of sewage treatment plants, neither with the bacteria nor the settling behaviour of the sludge [Opgenorth, 1992].

In a Zahn-Wellens test, more than 90% P((AA-MA) 70,000 were bound to the activated sludge after contact for only 2 hours. The practical elimination of PCA in sewage treatment strongly depends on the molecular mass and the acrylate/maleate ratio [Opgenorth, 1992]. P(AA) 1000 slowly undergoes biodegradation, while P(AA) 60,000 is eliminated > 96 % after coagulation using $FeCl_3$. Anaerobic biodegradation of PCA is also a slow process, but the PCA do not interfere with the biological processing of sludge and the degradation of other compounds.

PCA have little, if any effect on biota in the receiving waters [Alder et al., 1996]. Remobilization of heavy metals has been shown not to take place, and there is no acute lethal ecotoxicity found, even at concentrations > 100 mg/L.

## 2.5. Effects on washing efficiency and on materials

### 2.5.1. Properties and efficiency of the wash solution

STPP

According to the detergent industry and phosphate manufacturers, STPP provides a very efficient and well proven builder system. Among its important detergency properties are:

- Sequestering of hardness salts.
- Keeping hardness salts in solution.
- Removal and prevention of encrustation on the fibres.
- Dispersion of pigment soils.
- Synergistic intensification of the effect of anionic surfactants.
- Contribution to the alkaline reaction.
- Carrier for the other detergent powder constituents

Zeolite

When industry made the transition from STPP to other builder systems, Zeolite A turned out to be the core component of a builder system that could replace STPP. The effectiveness of Zeolite A in combination with PCA in the washing process has been examined in a number of basic investigations conducted by the detergent industry and zeolite manufacturers, and the main conclusion is that P-free detergents work quite well [Müller, 1996; Test (Berlin), 1996; Test Achats (Belgium), 1996]. Phosphate-free detergents and, in particular, the compact versions are considered to have led to considerable savings in detergent consumption [MoE Bonn, 1992]. The detergency properties of Zeolite A were investigated by Smulders & Krings [1990], Upadek et al. [1990], Upadek & Krings [1991] and Upadek et al. [1996], and their findings were:

- High binding capacity for multivalent metal ions, particularly calcium ions.
- Enhancement of the action of synthetic surfactants.
- Alkaline reaction.
- Anti-deposition properties (soil suspension power), particularly by adsorption of molecularly dispersed substances and heterocoagulation with pigments.
- Support of the foam depressing action of soaps.
- Crystallization surface for sparingly soluble compounds such as, for example, calcium carbonate.

- Increase of its effect by the presence of water soluble polycarboxylates or complexing agents (co-builder effect).
- High adsorption capacity for surfactants.

Except for the ability to act as a surface for crystallization of calcium carbonate and the better carrier capacity for surfactants, the detergency performance of Zeolite A is somewhat less than that of STPP. However, by adding co-builders such as citrate, phosphonates and polycarboxylates and by optimization of the surfactant system, zeolite-containing laundry detergents get a performance which is very similar to that of phosphate-based detergents [Christophliemk et al., 1992].

According to the detergent industry, it took a large effort and many technical adjustments had to be made before a new builder system approached the efficiency of the old. In most aspects, a builder system based on zeolite A/polycarboxylate or Zeolite P can be formulated to a similar performance level as phosphate based detergents using the same amounts of active ingredients.

Citrate

Because Zeolite A is an insoluble material, citrate is the most frequently used builder system for phosphate-free, heavy-duty liquid detergents. The primary function of citrate is to sequester water-hardness ions and thereby:

- Prevent formation of sparingly soluble magnesium and calcium salts of synthetic surfactants.
- Prevent formation of insoluble soap deposits that act as adhesives for particulate matter.

Typically citrate-built laundry detergents contain 5-10% sodium citrate, which has good compatibility with other detergent ingredients and is stable under normal washing conditions, even in the presence of strong bleaching agents such as perborate. Non-ionic surfactants do perform better with citrate than anionic surfactants, but frequently combinations of the two are used. Citrate is occasionally an ingredient in small quantities also in STPP and zeolite based detergents.

Higher dosage of zeolite or citrate based detergents?

The relative performance of zeolite based detergent systems with polycarboxylates, compared to STPP is subject to considerable debate. It is frequently stated by SCOPE that higher detergent dosage is needed for zeolite based detergents in order to obtain the same washing efficiency as with phosphate based detergents. If this was experienced by consumers, one would expect an increased consumption of detergents in the period from 1985-87 when P-based detergents became restricted in many countries. A study from 1988 confirmed an increased consumption by 15% (volume) after the exclusion of phosphate based detergents in Switzerland, but the overall trend in Western Europe is that the change of builder systems from phosphorus to zeolite based ones has not increased the consumption, see page 27 of Morse et al. [1994]. In Germany, there was a clear decline by more than 25% in detergent consumption from 1988 to 1995 [IKW, 1996], from 10.6 kg per capita in 1998 to 7.7 kg per capita in 1995. According to Kemira [1996], there has not been any general increase in the consumption of detergents for two reasons: The introduction of compact washing powders and the increased use of enzymes. Kemira claims that, in general, larger amounts of active ingredients in phosphate-free detergents have to be used. This has not been verified in recent tests by independent consumer magazines [IKW, 1996; Test (Berlin), 1996; Test Achats (Belgium), 1996]. Hauthal [1996] has shown how the dosage of detergents has decreased in Germany from 216 g/wash in 1986 to 76 g/wash in 1996. The amount of surfactants and soap has decreased from 27 g/wash in 1986 to 15 g/wash in 1996. This is the period in which phosphate-free detergents were developed in Germany.

Good knowledge of the hardness of the water is very important for correct dosing of the detergent. In soft water, there is no general need for increasing the dosage of a zeolite based detergent compared to a phosphate based one. However, in hard water, STPP provides a superior detergent builder system, implying that a larger increase in the dosage of zeolite detergent is needed. On the other hand, in hard water, there is a risk that $Ca_3(PO_4)_2$ may precipitate, if too little STPP based detergent is used. Therefore, STPP based detergents require larger dosages in hard water than in soft water [Kemira, 1996]. The same is true with citrate based detergents. Apparently, zeolite based detergents could be dosed more independently of water hardness [Test (Berlin), 1996].

Citric acid based systems may be superior to the other two systems in cold water. One mole of citric acid binds one mole of calcium at 25°C, while 2/3 of a mole of calcium is bound at 50°C [Hoyt & Gewanter, 1992].

Table 2 presents of the most frequently used detergents in Sweden. The dosage recommended for soft water washing of 3 – 4 kg of laundry is included. The dosages that were used in the 'Stockholm Vatten' study [Wahlberg, 1995] are also given

**Table 2. Recommended dosages for different detergents.**

| Detergent | Builder system | Råd & Rön dosage[Å] | Stockholm V. dosage[Ç] | Surfactant amount[Ç] |
|---|---|---|---|---|
| *Detergent powders with bleaching agents:* | | | | |
| Absolut Rent, Bastvätt | Phosphate, silicate | 50 ml[É] | | |
| Emanco Accent | Phosphate | 50 ml | 43 g (75 ml) | 7 g(20%) |
| G48 Vittvätt | Phosphate | 50 ml | | |
| Tellus Bastvätt | Phosphate | 45 ml[Ñ] | | |
| Absolut Rent, kulörtvätt | Silicate | 50 ml[É] | | |
| Via Power | Zeolite | 50 ml | 65 g (175ml) | 13 g (20%) |
| Tend Compact | Zeolite, polycarboxylate | 67 ml | 98 g (133 ml) | 20 g (20%) |
| Ajax Ultra | Phosphate | 50 ml[Ñ] | 72 g (93 ml) | 11 g(15%) |
| Ariel Futur | Zeolite, polycarboxylate | 70 ml | 62 g (90 ml) | 12 g (20%) |
| Skona Kompakt | Phosphate | 75 ml | 83 g (125 ml) | 19 g (20%) |
| Mini Risk Kompakt | Zeolite, polycarboxylate | 75 ml | 92 g (135 ml) | 18 g (20% |
| Skona Colour | Zeolite, polycarboxylate | 75 ml[Ö] | | |
| Änglamark | Citrate, polycarboxylate | 75 ml | 75 g | |
| Nopa Compact Ultra | Phosphate | 90 ml | 77 g (135 ml) | 12 g (20%) |
| Via TAED 6040 | Phosphate, polycarboxylate | 100 ml | 104 g (150 ml) | 16 g (20%) |
| *Detergent powders without bleaching agents:* | | | | |
| Absolut Rent, bastvätt | Phosphate, silicate | 50 ml | 42 g (75 ml) | 6 g (15%) |
| Absolut Rent, kulörtvätt | Silicate | 50 ml | 63 g (100 ml) | |
| Emanco Kulör | Zeolite, polycarboxylate | 50 ml | | |
| Expert | Phosphate | 50 ml | 52 g (100 ml) | 8 g (20%) |
| G48 Kulörtvätt | Zeolite, citrate | 50 ml | 83 g (100 ml) | 17 g (20%) |
| Via Color | Zeolite | 50 ml | 68 g (75 ml) | 14 g (20% |
| Tend Color | Zeolite, polycarboxylate | 67 ml | 102 g (183 ml) | 20 g (20%) |
| Ajax Color Kompakt | Phosphate | 50 ml[Ñ] | 66 g (93 ml) | 10 g (15%) |
| Ariel Futur Color | Zeolite, polycarboxylate | 45 ml[Ñ] | 66 g (90 ml) | 12 g (20%) |
| Skona Color | Zeolite, polycarboxylate | 75 ml | 92 g (160 ml) | 18 g (20%) |
| Änglamark Kulör | Citrate, polycarboxylate | 75 ml | 75 g | |
| Ecover Kompakt | Zeolite, citrate | 80 ml | 85 g (125 ml) | 17 g (20%) |

Source: KTF.
[Å]Test from Råd & Rön [Farm, 1994].
[Ç]'Stockholm Vatten' study [Wahlberg, 1995].
[É]+ 15 ml bleach salt.
[Ñ]New formulations.
[Ö]+ 45 ml bleach salt.

for those detergents that were studied. From Table 2 it is clear that the general statement

> "zeolite based detergents require a larger dosage than phosphate based detergents"

is not generally valid.

It is not an inherent property of a phosphate-free detergent builder that larger amounts of surfactants must be used to achieve a similar washing performance level as that of a STPP-based detergent [Hauthal, 1996; Test (Berlin), 1996; Test Achats (Belgium), 1996].

Although the recommended dosage of zeolite based detergents presented in Table 2, in several cases, is higher than the recommended dosage of phosphate based detergents, there are several low-dosage phosphate and zeolite based detergents available. Also among the high dosage detergents there are both phosphate and zeolite based ones. Thus, different washing powders may be difficult to compare as some of the new formulations are more advanced than the older ones; new enzyme systems are introduced etc. Also, the market share of the different brands in Table 2 varies a great deal, so the dosages presented in the table do not reflect the actual consumption of surfactants in Sweden.

Liquid detergents are often based on other builder systems than zeolite and phosphate and are therefore not included in Table 2. Citrate based builder systems are most frequently used in liquid detergents as exemplified in Table 1. Seemingly, the relative amount of surfactants in these formulation is larger than in the case of zeolite or phosphate based builder systems. However, a low consumption of surfactant per wash is possible for both STPP based and zeolite based detergents, if certain brands are used with their recommended dosages, Table 2.

Washing efficiency

According to Constant [1992] the washing efficiency can be split into:

- Stain removal:
  - Proteinic stains removed by enzymes, and
  - Oxidizable stains removed by the bleaching system.
- Soil removal
  - Grease and dirt from the fabric.
- Encrustation
  - Undesirable build up of deposits on fabrics.

Generally, stain removal is independent of the builder system, while soil removal and encrustation are dependent on it. In one study, Constant [1992] was able to show in actual tests that a P-based detergent could be dosed in an amount of 45% less than a compact zeolite based detergent for an equivalent soil removal ability, while the stain removal capability was the same at equivalent dosage. The level of encrustation was 75% lower using the P-based detergent compared to the zeolite based detergent at equivalent dosage. This result is in contrast to newer independent tests showing excellent performance of modern zeolite based detergents [Test (Berlin), 1996; Test Achats (Belgium), 1996]. The consumption of detergent per wash has decreased, in general in Western Europe during the last decade [Hauthal, 1996; IKW, 1996].

In many studies of the environmental impact of detergents, the soil removal capability has been used as a dosage criterion for "equivalence of performance", rather than stain removal or manufacturers' recommendations. According to Kemira [1996] this is because stain removal is regarded as a bleach/enzyme issue and not greatly influenced by builders, which are better evaluated by measuring soil removal capacity and amount of encrustation. Therefore, elevated levels of COD, BOD and TSS in the effluent have been reported in laboratory studies more on the basis of differences in dosage than on differences in formulation, e.g. [Johnston, 1992; Leal, 1992; Scholten et al., 1994]. Few of these studies can be used to assess the difference in environmental impact of zeolite and phosphorus based detergents in the real world, where consumers don't use more detergent, in general, when shifting to zeolite builder systems. However, the formulation of a Zeolite A based system does require a larger fraction of organic carbon, and therefore, differences do exist in favour of the Zeolite P or STPP based systems (neither of which require PCA) , in terms of lower COD and TSS values in the washing effluent [Chambon, 1992].

### 2.5.2. Residues deposited on textiles

Zeolite

A Finnish study has been conducted by the Consumer Department in co-operation with the Work Efficiency Association and the Textile and Foodstuff of Laboratory at the Technical Research Centre of Finland [Kuluttaja (The Consumer), 1995]. Results from this study indicate that insolubles (i.e. zeolite) make textiles hard, change colours and reduce the brightness and resistance to wear [Kaarina Kuusimaa, 1995]. Granules left on the laundry became grease stains on the bed-sheet during mangling. The residues found in the fabrics after washing were reported to be zeolite particles, surfactants, phosphates, chloride and silicates—dependent on the detergent used. Electron microscopy showed that phosphate free detergents left approximately ten times the amount of residual particles compared to phosphate based detergents [Kemira, 1994]. As this could potentially cause skin irritation, the consequence was that zeolite containing detergents could not be used any more in commercial Finnish laundries.

However, the number of rinsing cycles and the amount of water greatly influence the amount of residues. Correct dosage and correct use are more critical with compact detergents, in general, especially with respect to reduced water levels in modern machines. Compact detergents should not be overdosed and the machines should not be overloaded with laundry [P&G, 1994].

As mentioned, zeolite particles are suitable substrates for crystallisation of sparingly soluble compounds, e.g. calcium carbonate or calcium phosphate [Christophliemk et al., 1992]. If the detergent is overdosed, zeolite particles may be left as particles on the textile fibres and the deposits can be perceived as encrustation after repeated washing. Therefore, correct dosage according to the prescription given on the package is very important—more so for compact than for regular detergents.

Citrate

Apparently, the same experience with more particles on the fabric has not been experienced with citrate as a builder. Citrate is a very good builder at low temperatures, but generally larger amounts of surfactants are required in the formulations as compared to STPP and zeolite based detergents. This becomes a cost problem, i.e. citrate based systems are roughly 10% more expensive to produce at the same performance level. It has been speculated that surfactants, or their break-down products, can deteriorate the quality of the biosludge at the municipal sewage treatment plants, and if that turns out to be true, there is also some environmental implications of the citrate builder system. However, there are few hard facts and much speculation at this point in time. In my opinion, the abundant use of coagulants at Swedish sewage treatment plants could cause the kind of disturbances that have been observed, particularly if excess amounts of free coagulants are recirculated with the activated sludge to the primary settling tank or the aeration basin. This would create a lack of bioavailable phosphorus for the growth of activated sludge. If discharged without biological treatment, surfactants are known to have a negative environmental impact [Scholten et al., 1994].

### 2.5.3. Residues in washing machines

Dependent on choice of builders?

Speculations have come up regarding the possibility that since zeolite is an insoluble particle and therefore requires a good rinsing programme in the washing machines, it also precipitates more easily as a calcareous mass on the inside of the washing machines than compounds of STPP based detergents may do. The Finnish Work Efficiency Institute has studied the problem and speculated that precipitates may cause damage to washing machines. It is a fact that:

- The reduced water volumes used in modern washing machines compared to older models can increase the level of residues, unless suitable precautions are taken.
- However, there is no evidence of any difference between phosphate and phosphate free detergents with regard to the level of residues in washing machines [Konsumentverket, 1996].

The Swedish “Konsumentverket” informed at a meeting in Stockholm [Konsumentverket, 1996] that consumers reported increasing problems with:

- Bad smell of the fabric after washing.
- Coatings on the fabric.
- Yellow stains on the fabric.
- Mould in the (detergent inlet of the) washing machine.
- Dust particles in the fabric.
- Calcareous mass on the inside of the washing machine.

At the meeting, those problems were reported to occur with all brands of washing machines and with all types of detergents, but the “Konsumentverket” speculated that zeolite based and compact detergents were more involved than STPP based detergents. A total of 50 complaints were reported to have been made to the “Konsumentverket” after a television documentary focused on these issues (the “Plusprogram”), so the “Konsumentverket” regarded the problem as being relatively serious. However, the “Konsumentverket” was not able to give any detailed statistics on the issue, neither were they able to share any information regarding the details of those complaints to facilitate a more thorough analysis of the problem. The audience at the seminar included detergent manufacturers as well as washing machine manufacturers. The detergent manufacturers could not confirm that an increasing number of complaints was recorded in recent years. It was concluded that:

- The magnitude of the above problems is not well quantified.
- Several factors rather than a single one are involved in the causes of the problems.
- Multiple washings at low temperatures (25°C – 35°C) are believed to be a major cause of the above problems.
- Less water usage, new builders and new surfactants are believed to be of less importance than low washing temperatures.
- Lots of speculations were presented, e.g. that certain skin lotions and hair restorers could be involved.

Conclusion

If the magnitude of the problem justifies any further studies, a good data base of complaints needs to be established, including detergent brands, machine brands, water hardness, geographical areas, family types etc. A statistical analysis of this data base should be developed, before resources are allocated to anything else. So far, it has not been demostrated that the detergent builders are a main cause of any of those problems.

### 2.5.4. Increased washing machine wear?

Early studies published in 1983 reported problems with increased washing machine wear, leading to premature disposal of washing machines, replaced parts and increased maintenance in Western Europe and USA [Morse et al., 1994]. However, these problems were probably related to older formulations. Today, after several life time tests on washing machines [Test (Berlin), 1995], there is no concern among machine manufacturers for possible adverse impacts of zeolite based detergents on washing machine durability. The machine manufacturers referred to statistics at the Stockholm meeting [Konsumentverket, 1996], showing no increase in mechanical problems with new machines, e.g. the service on water pumps were at a constant level, which would not have been expected had the calcareous mass on the inside of the washing machine been an increasing problem.

Our impression at the Conference was that, if a consumer has problems with residues in the washing machine, it is most likely a better cure to dose the detergent correctly and to wash at temperatures between 40-50°C, than to change the brand of detergent.

### 2.5.5. Energy comsumption

In LCA studies of detergents, the washing temperature used in the households is often claimed to be the most important energy parameter. Detergents that are able to wash efficiently at lower temperatures are often regarded as the most efficient ones. However, all detergents can cause encrustation or build-up on the heating element of washing machines and thereby decrease the thermal efficiency. Residues (of particles) are more pronounced at very low (<30°C) temperatures, whereas encrustation (by sparingly soluble salts) is more pronounced at very high (>60°C) temperatures. Thus, washing between 40° - 60°C is generally recommended. Washing at < 30°C requires more detergent or gives rise to a poorer wash result [Andresen, 1996]. There seems to be no difference between the STPP and the zeolite based detergents in this regard.

# 3. Effects on sewage treatment plants

Background

As a consequence of operational disturbances observed at Swedish municipal sewage treatment plants during the past five years, IVL presented results from a newly published study [Frostell et al., 1995] at a recent seminar [SIS Miljömärkning, 1996].

The operational disturbances consisted of:

- Increased discharges of suspended solids.
- Impaired sludge quality:
  - Increased sludge volume,
  - Increased number of filamentous bacteria.
- Pronounced tendency of sludge foaming.
- Colour changes of the sludge, which is often an early warning of problems.
- Operational problems, particularly:
  - During the cold seasons, and
  - For small and medium sized plants.
- Other problems.

The study points to a change in the use of chemical products as the most plausible cause of problems:

- New household chemicals, e.g. P-free detergents.
- New formulae for automatic car washing installations.
- New industrial chemicals, e.g. aqueous degreasing of metals instead of using trichloroethylene leads to a greater discharge of oil, grease, soap and surfactants.

Add to that:

- Water savings—more concentrated effluents.
- Water based paints increasingly end up in the sewage.
- Many other chemicals that potentially could cause problems.

- New wastewater treatment processes
  - Nitrification requires high sludge ages and the foaming tendency of sludge often increases as the sludge age increases.
  - Denitrification requires anoxic zones.
  - More advanced sludge treatment processes.
  - Filamentous sludge that increased the sludge index.
- Soft water—a characteristic of Northern Scandinavia—increases foam stability.

Thus, the study by Frostell et al. [1995] documents increasing operational problems at Swedish sewage treatment works, but provides no evidence as to the cause of these problems. Phosphate-free detergents have been used for 20 years, e.g. in Germany and Switzerland and for the past 10 years they have been used exclusively, e.g. in Switzerland. They have not been blamed for any adverse effects on sewage treatment plant performance in those countries [MoE Bonn, 1992; Siegrist & Boller, 1996].

Fatty acids?

At the seminar [SIS Miljömärkning, 1996], one of the speculations, which was elaborated in some detail, was the potential of the increasing fatty acid discharges to be a key parameter for these disturbances.

The concern about fatty acids was raised by operators of several Swedish treatment plants, e.g. at Klippan and Gävle. They claimed that the problem of foaming and less efficient oxygen transfer had increased during the last 3 – 5 years. It was speculated that the cause of the problem could be the increased discharge of surfactants due to the new builder systems in detergents. However, in 1979, a detergent contained 8.3 g/wash of soap, in 1986 the figure was reduced to 2.2 g/wash and in 1996 a super compact detergent contains 0.7 g/wash of soap [Hauthal, 1996]. Figures for consumption of surfactants have also decreased (cf. Table 2, where it is shown that 2 of 3 new detergent formulations contain only 15% surfactants, as compared to most other detergents containing 20%).

According to Prof. Henze, Danish Technical University, foaming problems have increased in Europe during the last 5 - 10 years, but the cause remains obscure—there are few facts and many speculations. Normal sewage contains 10% (d.w.) fatty acids (free or bound as triglycerides or otherwise), so it is hard to see that an additional small load from surfactants that breaks down to form fatty acids could be the cause of the problem. 7.9 mg/L of fatty acids have been estimated in raw sewage in The Netherlands as coming from detergents (which is 28% of the total load of 28 mg/L); 99% was removed in the activated sludge process [Feijtel & van de Plassche, 1995].

However, the chemical nature of surfactants may have changed the composition and availability of fatty acids during sewage treatment, and it cannot be ruled out that this can be part of the problems experienced in Sweden during the past five years. The chemical nature of surfactants has been altered during the past decade away from slowly degradable surfactants towards readily degradable ones, but there are no direct studies to support the hypothesis that this has caused problems in sewage treatment.

In Switzerland, where P-based detergents have been banned for the longest period of time, up to now no foaming problems have been detected due to P-free detergents [Siegrist & Boller, 1996].

## 3.1. The 'Stockholm Vatten' detergents study

The study by Wahlberg [1995] was initiated to address concerns that new compact detergents, if overdosed, could give rise to adverse effects in the environment, and in particular that the environmental benefits of compact detergents, if overdosed, were minimal.

The aim of the Wahlberg study was i.a. to study the environmental impact and the impact on wastewater treatment plants (e.g. nitrification) of different laundry detergents mixed with sewage. Another aim was to compare the environmental compatibility determined by chemical and biological analyses of 27 detergents of different types, e.g. STPP based, zeolite based etc. The study comprised 20 powdered detergents (including 7 phosphate based and 9 zeolite based detergents) and 7 liquid detergents.

Experimental design

Washing waters from these detergents were analysed for:
Chemical parameters

- COD
- $BOD_7$
- TOC
- DOC
- pH
- tot-P
- SS.

Ecotoxicological parameters:

- Microtox®
- Growth inhibition of green algae (*Selenastrum capricornutum*) (3 samples).
- Inhibition of nitrification processes.
- Degradability tests
  - Microtox on stabilized samples
  - COD on stabilized samples
  - $BOD_7$ on stabilized samples
  - TOC on stabilized samples.

The study is in many aspects inconclusive due to its design. This has been discussed in more detail elsewhere [Folke, 1995].

Recommendations

The study led to a recommendation by Stockholm Vatten to use phosphate containing detergents. The recommendation was mainly based on the conclusion that the detergent phosphate added to the chemical sludge would be advantageous, if the sludge was spread on agricultural land. However, this is an oversimplification. It is well documented that nutrients in sewage sludge are available to plants [Valdmaa, 1986; SYSAV, 1992], but the initial effect of chemically precipitated phosphorus in sludge is limited, particularly if the pH of the soil is low, in which case phosphorus is tightly bound by aluminium ions [Kyle & McClintock, 1995; Madsen, 1996]. For example, in Denmark, sludge is often applied on municipality leasehold land, and if the main purpose would have been to fertilize the land, liming would be more efficient than adding further phosphorus to an already large phosphorus pool in the soil [Madsen, 1996]. Furthermore, phosphorus is well over 100 times more available to plants when applied as mineral fertilizer or as sludge from biological phosphorus removal processes as compared to sludge from alum of ferrichloride phosphorus removal processes [Kyle & McClintock, 1995]. Thus, phosphorus from the latter processes does not have the same beneficial starter value as phosphorus from biological P-removal. Consequently, the increased fertilizer value of chemical sludge containing additional phosphate from P-based detergents, when spread on agricultural land, is not alone enough to justify a broad recommendation of using P-based detergents. It really depends on the local conditions. The question is rather, whether the use of STPP in detergents should be limited on the basis of phosphorus being a limited resource [Zehnder, 1996].

Liquid detergents were found to contain almost 7 times as much $BOD_7$ as the phosphate or zeolite containing detergents. This was claimed to cause increasing energy demand and to increase the amount of sludge created. However, it was concluded that the fraction of the $BOD_7$ that was made up by citrate, ethanol and propylenglycol could improve denitrification and biological phosphorus removal. The results were inconclusive with regard to the ability of surfactants to assist in the denitrification [Folke, 1995].

## 3.2. P-free detergents

SCOPE and some of the companies behind this committee have published newsletters and press releases that initially raised the concern that phosphate-free detergents may create disturbances at wastewater treatment plants by statements such as:

- It is unknown how non-P based builder systems affect the treatment processes.
- Zeolite based detergents, in particular, cause problems for treatment plants, e.g.:
  - Foaming problems,
  - decreased oxygen transfer efficiency in aerators,
  - increased sludge loading,
  - this sludge is more difficult to use in agriculture (because the P-concentration is lower?).

The majority of these statements on adverse effects are directed against zeolite rather than against citrate builder systems.

The Swedish VAV (Federation of Water and Sewage Treatment Works) has speculated that zeolite based detergents cause problems for sewage treatment plants [SCOPE, 1992].

Most of these concerns are currently under investigation and not yet documented.

Zeolite

Zeolite A does not cause any excessive clogging of domestic waste water in piping systems. Field trials have shown that zeolite contributes no more than 5% to the sediment in horizontal pipes [Christophliemk et al., 1992]. About 66% of the zeolite is separated and incorporated into the sludge of the primary clarifier. After passing the clarifier, 96% are separated from the effluent. According to field trials, only 4% leave the plant with the final effluent [Christophliemk et al., 1992].

In the Landbank Report [Wilson & Jones, 1994], results from laboratory and small scale pilot plant experiments are reported, showing that around 50% of the zeolite are separated after primary clarification and 90% after secondary treatment. The remaining 10% are discharged. In the report by Morse et al. [1994] results of various studies are presented, where the zeolite removal ranges from 55% to 77% after primary treatment. After secondary treatment removal rates between 80-90% were observed.

According to a review by ECE [1980], zeolite concentrations of up to 60 mg/L had no adverse effects on the purification performance in terms of BOD-removal. No adverse effects on anaerobic sludge digestion or excessive clogging in piping systems were shown, i.e. zeolite had not been shown to have any negative influence on the treatment process at the sewage plants [Naturvårdsverket Informerar, 1992; Kemikalieinspektionen, 1994]. It had also been shown that the mass of the sludge increased, but the volume only increased slightly with zeolite based detergents. Addition of zeolite caused increased sludge retention and enhanced nitrification. Futhermore, zeolite addition resulted in a decreased sludge index, easier dewatering of the sludge and hence an increased treatment efficiency and consequently increased sludge mass loads, i.e. 10-15% on dry matter.

In activated sludge treatment, Zeolite A occasionally improves the removal of certain metals (zinc, copper and chromium), but the positive influence of zeolite on the removal of heavy metals is of no practical importance [Morse et al., 1994]. The improved nitrification observed at zeolite application is probably due to increased sludge retention resulting in improved sludge age [Christophliemk et al., 1992].

The ultimate fate of zeolite in wastewater treatment is incorporation into primary and secondary sludge. Therefore, its influence on anaerobic processes is of importance. Several investigations yielded no indications of adverse effects in this regard, even if heavy metals were bound to zeolite [Christophliemk et al., 1992].

No adverse effects on process efficiency or effluent concentrations of trace metals were found in investigations on the impact of zeolite on laboratory septic tank systems, full scale septic tanks or small scale aerobic systems in the field. Zeolite removal rates in these systems were reported to be between 81 – 88% [Morse et al., 1994].

In Switzerland, zeolite detergents are regarded as advantageous due to a reported better P-removal efficiency in addition to a lower chemical dosage needed for simultaneous P-precipitation [Siegrist & Boller, 1996]. An effluent concentration of 0.6 mg P-tot/L can be achieved with a Fe/P-tot-ratio of about 1.5. The P-removal efficiency by incorporation into biomass through growth increased from 15 to 35% related to the P- load in the primary effluent. Biological P-removal was reported to be more stable and additional chemical P-precipitation significantly lower, when zeolite was present in the raw sewage.

In conclusion, zeolite has no adverse effects on the biological treatment processes and there are no facts to support that the observed decreased oxygen transfer efficiency in aerators has anything to do with zeolite. Zeolite increases sludge loads by 10-15 %, but at the benefit of a better sludge quality and thus improved wastewater treatment. Zeolite itself is inert to plants and other living organisms when spread on agricultural land. On hydrolysis, silica and aluminum ions are liberated, and the latter could potentially cause a problem in connection with acid rain, but I have not identified studies analysing this aspect.

PCA

As previously mentioned, polycarboxylates are normally used in Zeolite A based detergents. An unpublished $^{14}C$ labelled study of the P(AA-MA) 70,000 behaviour in activated sludge treatment, referenced by Opgenorth [1992], and ECETOC [1993], showed that only 2-3% of the activity were found in the discharge, i.e. that 97-98 % were eliminated. Similar high removal rates were only found for lower mass PCAs, if iron salts were added (to control phosphate discharge). Unpublished results by BASF were also referenced to show that PCAs in concentrations relevant to their use in detergents do not interfere with the operation of treatment plants , i.e. the activity of bacteria in activated sludges was not adversely affected by the presence of PCAs. The mobility of heavy metals was not affected[5], and there was no effect on the phosphorus precipitation and the dewatering of excess sludges [Opgenorth, 1992].

PCAs are slowly degradable both under aerobic and anaerobic conditions. P(AA-MA) 70,000 has been shown to remain adsorbed in anaerobic towers and not to interfere with the anaerobic activity [Opgenorth, 1992].

[5] PCA has such strong affinity to calcium that its ability to mobilize e.g. heavy metals is minimal and not documented.

Citrate

Citrate is involved in the intracellular metabolism of most organisms and is found in almost all living systems. Humans also excrete citrate, so raw sewage contains 0.1 – 5.3 mg/L of citrate with a median of 1.5 mg/L [Hoyt & Gewanter, 1992]. Activated sludge treatment reduces the level to < 0.1 - 1.4 mg/L with a median of 0.2 mg/L (> 82% removal).

Assuming that a detergent contains a maximum of 25% by mass of a builder, and that all detergents were citrate based, the raw waste concentration would be $10 \times 10^6 / 365 \times 0.25 / 200 \approx 34$ mg/L, which is thus a theoretical maximum. Several food processing industries have discharges of up to ≈ 30 mg/L [Hoyt & Gewanter, 1992]. In one well documented case, the Frederikssund Municipal Sewage Treatment Plant, this discharge proved to be of great advantage in the biological denitrification and phosphorus removal processes [Anonymous, 1994]. Even if biological nutrient removal is not practised, citrate will be degraded by any biological process without any need for adaptation. And if it should end up in sludge applied on agricultural land, it will easily be degraded.

Therefore, citrate cannot be claimed to cause any problems for sewage treatment plants—on the contrary, it will improve the process of nutrient removal by acting as a useful C-source.

## 3.3. P-based detergents

STPP increases the level of phosphate in raw sewage, primarily in the form of orthophosphate. According to the SNV Report 4429, the contribution of phosphorus from humans into sewage in Sweden is 2.1 g/person/day—1.5 g/person/day is from urine and feces, and 0.45 g/person/day is from phosphorus based household products. Full use of STPP based detergents is estimated to increase the total amount to 2.5 g/person/day, i.e. 34% would come from phosphorus based household products.

As previously mentioned, several operators of Swedish sewage treatment plants publicly state that they prefer phosphate based detergents because:

- Uncertainty about how the phosphate substitutes influence the treatment process,
- Phosphorus is an important nutrient for micro-organisms in the treatment process, and
- Phosphates are easy to separate.

SCOPE has claimed that phosphate based detergents are preferential because:

- Phosphate based detergents contain smaller amounts of surfactants and these are more easily biodegradable than those in zeolite based detergents,
- Phosphorus is needed as a nutrient for micro-organisms in the treatment process,
- Phosphates are easy to separate from the effluent.

However, some of these arguments are questionable from a technical stand-point, e.g. that phosphorus from detergents is needed in the treatment process, or that they are easily separated from the effluent. Phosphorus is plentiful from other sources, and special technologies are needed to separate phosphate from the effluent. However, it is true that phosphate based detergents have a long record of causing no problem during sewage treatment. The technologies for the removal of phosphate from sewage are well demonstrated, including chemical coagulants as well as biological phosphorus removal processes. After primary treatment 5-15% of the phosphorus are removed. Measurements made on phosphorus removal in secondary treatment ranges from 10-30% to 20-40%. With a tertiary level of treatment, phosphorus can be removed to almost any desired level (typically 90% or more).

Phosphorus levels in raw sewage are in considerable excess of what is needed for biotreatment, even if P-free detergents were used exclusively. Any increase in the raw sewage P-loading from P-containing detergents will have to be removed through (additional) tertiary treatment, as the normal P-load from other origins is assumed to already exceed the removal capacity of the primary and secondary systems. But phosphate removal techniques generally work so well that the effluent concentration of phosphorus solely depends on the application of specific techniques rather than on the influent concentration. As mentioned, normal raw sewage from households contains sufficient phosphorus as each person is estimated to discharge more than 2 g P/day in 200 L water, i.e. >10 mg/L. So, the claim that STPP based detergents are of any particular benefit to the biological treatment process is not true. It costs extra money to remove extra phosphate—unless may be, if the phosphorus removal is solely achieved through biological processes. It costs extra money to remove zeolite as well because of the increased mass of sludge, but less so than the extra money to remove phosphate [Hasling et al., 1990]. According to Hasling et al. the cost of treating easily digestible

**Table 3 Fraction of the EU population connected to sewage treatment plants with primary, secondary, and tertiary treatment.**

| | Primary | Secondary | Tertiary |
|---|---|---|---|
| EU (< 1994) | 8% | 48% | 9% |
| Finland | 0% | 0% | 100% |
| Norway | 26% | 1% | 72%[Å] |
| Sweden | 0% | 5% | 90% |
| Switzerland | 0% | 0 % | 90% |

[Å]56% of those are without biological treatment.
Source: [Morse et al., 1994]; amended after [Kemira, 1996].

BOD (e.g. from citrate-based detergents) is trivial compared to the cost of sludge handling.

Only 9% of the population in the EU (before Austria, Finland and Sweden joined) were connected to wastewater treatment plants with tertiary treatment in 1994, see also Table 3. This table shows that Sweden may have the capacity to handle P-based detergents. However, according to Landner from MFG-S 1.15 mill. Swedes in 1994 were not connected to sewage treatment plants at all. It is not clear how this fact has been incorporated into Table 3. One could imagine that a similar proportion of the Finnish and Norwegian population were unconnected. The continental EU countries represent a great variation, where Denmark, Germay and the Netherlands have in a very high percentage of its population connected to advanced sewage treatment plants, while the southern countries of the EU have little, if any tertiary treatment at all. The situation is expected to improve drastically during the next couple of years. Local conditions are of course important when comparing countries, e.g. in Norway, the ocean outfall gives a very different situation from e.g. the Swedish one.

Surfactants

In the development of compact and super-compact detergents, builders have been used to substitute quite a large fraction of the surfactants, so these detergents can be formulated to contain smaller amounts of surfactants than was the case a decade or two ago [Hauthal, 1996]. It has taken a considerable effort to develop zeolite and citrate based builder systems that are as efficient as STPP, and citrate-based detergents generally contain a larger fraction of surfactants. However, the surfactants used in modern detergents are essentially of the same nature in all cases.

## 3.4. Costs for sewage treatment

According to the P&G European Technical Centre [Schowanek, 1996], the effluent loading from washing machines in an average municipal effluent constitutes:

- Approx. 10% - 15% of the organic carbon (measured as DOC)[6]
- Approx. 1% of the total nitrogen
- 3% of the total phosphorus, if zeolite or liquid, P-free detergents are used—
  35% of the total phosphorus, if P-containing detergents are used.
- Approx. 2% of the total effluent volume[7].

Böhnke et al. [1992] estimated that 14% of the operating costs for a municipal sewage treatment plant was due to the use of detergents. In particular, the handling of solids in the detergents that ended up in the sludge was a heavy cost factor, much more so than the BOD:

Relative treatment cost

- Surfactants 3.3 %
  Anionic, nonionic
- Builders, except for citrate 9.4 %
  Phosphate, phosphonate, zeolite, polycarboxylate
- Bleaching agents 0.4 %
- Other constituents 1.0 %

Unless biological P-removal is practised, the removal of additional phosphate is more expensive than the removal of additional zeolite due to the need for coagulant chemicals.

Sewage pipes and sludge

A Danish research project from 1990 assessed the consequences of treating carbon rich industrial effluents in municipal treatment plants [Hasling et al., 1990]. First of all, the value of a sewage pipe system by far exceeds any value of the corresponding treatment system. Municipalities generally pay much too little attention to this when budgeting operating costs and maintenance. The cost of the sewer system is mostly dependent on the volume of water. Secondly, the cost of sludge handling systems at a municipal treatment plant is the largest

[6]The average annual consumption of detergent per capita is approx. 10 kg. ≈50% of the 10 kg is organic material and ≈50% of this is organic carbon, i.e. ≈2.5 kg/y. The annual water use is 365 days/y x 200 L/d = 73,000 L/y, so DOC ≈35 mg/L. An average domestic effluent has a DOC of 200-400 mg/L, so detergents contribute 10-15% of the DOC [Schowanek, 1996].

[7] Water consumption is 200 L/d/capita. 1 washing is ≈ 20 L; assuming 1-2 washes a week/capita.

investment (≈60% of the capital for building a total biological treatment plant). Thirdly, cost factors varies according to the design of the sewage treatment system. BOD is most efficiently removed in secondary treatment according to a cost efficiency study conducted [Ødegaard, 1995]. The study by Henze & Ødegård pointed to the fact that costs for removal of 1 kg of BOD or SS (i.e. citrate or zeolite respectively) are 20 – 30 times cheaper than the costs for removal of 1 kg tot-P. Generally the costs of chemical pre-treatment for SS and tot-P removal came out more favourable than costs for removal in biological treatment. Hasling et al. [1990] found no increasing cost, but in fact a small cost reduction for treating a soluble BOD in the influent, if the treatment system was designed for biological nutrient removel—provided that the organic carbon in the influent $BOD_{sol}$ can be used efficiently for denitrification purposes. The capital cost breakdown for a municipal treatment systemwith bioligical nutrient removal was estimated to:

| | | |
|---|---|---|
| Basic costs | = | 40% |
| Q | = | 32% |
| BOD | = | 6% |
| Tot-N | = | 11% |
| Tot-P | = | 11% |

The basic costs include sludge treatment, but not final sludge handling. Treatment plants are now being built all over Europe to introduce secondary and tertiary treatment of wastewater from cities. Therefore, the amount of biosludge is increasing, and the cost of final sludge handling can be foreseen to increase as well.

Biosludge

The biosludge from treatment plants can be used on farmland, if the content of heavy metals and xenobiotic, organic compounds are not too high. Alternatively if allowed, the sludge can be burned and go to a landfill. In some instances, it goes directly to a landfill without burning. The extra amount of sludge from zeolite or phosphorus removal will, in most cases, increase the costs of sludge handling and landfills are a limited resource all over Europe in case the sludge cannot be spread on land. However, as the presence of zeolite in sludge may increase the dewaterability of the sludge, the actual cost of sludge handling can also go down, if the cost is calculated by wet volume of sludge. Alternative sludge handling systems (i.e. incineration) to the current practice of spreading on agricultural land are seriously under consideration by many Danish municipalities following the new Danish guideline for contents of certain xenobiotics in biosludge. Denmark has submitted a proposal to the EU Commission to adopt this guideline for all of Europe.

# 4. Health aspects

Neither of the three builder systems gives rise to concern regarding toxicity. Citrate and phosphate are part of the metabolic system of any living organism and zeolite is quite inert to biological systems.

## 4.1. STPP (Phosphate)

The oral toxicity of STPP is very low, $LD_{50}$ (rat) = 3.2 g/kg. It has no demonstrated irritant properties, and it is not a carcinogen, mutagen or teratogen. Phosphorus is essential to life and is present in the human diet at around 0.7 kg/capita and year.

Therefore, there is no concern for any adverse health effects in using STPP as a detergent builder.

## 4.2. Zeolite

Zeolite A is basically non-toxic to living organisms including man. Oral dosage of 5 g/kg in rat had no effect, while 10 g/kg for 90 days produced some effects such as urinary bladder stones and increased Si content of the kidney [Christophliemk et al., 1992].

Zeolite A is classified as a neutral dust in the workplace (MAK = 6 mg/$m^3$), and it does not contribute to cancer or lung diseases. Contrary to other zeolites the uniform octahedron structure of Zeolite A makes it inert. Thus zeolite A does not pose a health hazard, either at the workplace or as a component in household chemicals [Christophliemk et al., 1992].

Risk of allergy from traces in textiles?

Inappropriate use of zeolite based detergents, e.g. under- or overdosing, inadequate rinsing after wash, reduced water levels, too hot or cold temperatures etc., gives a higher risk of residues in the fabric and washing machines than other builders as discussed earlier on page 23 [Matthies et al., 1990]. As opposed to STPP and citrate/fatty acid builder systems, zeolite builder systems contain more insolubles, so the effect of inadequate use may become more evident in terms of coatings on the fibres, as illustrated by Kemira [1994]. The higher ash content demonstrated in this study after washing with zeolite based detergents has led to a speculation that this may lead to a greater exposure to allergens that may be present in the fabric as part of the fabric or as dirt.

A pilot study on possible adverse effects of a Zeolite A detergent has been conducted in Finland, but no conclusions on the possible hazards of residual particles could be made [Kuluttaja (The Consumer), 1995]. The hypothesis was that pollen, animal dust or some anionic surfactants, suspected of causing allergenic reactions, could be brought in contact with sensitive persons through mechanical irritation of the skin by zeolite. However, Zeolite A has been tested for skin and mucuous membrane compatibility and sensitisation, and this did not show any substance-related effects. Apparently, the general opinion among dermatologists is that silicate residues in textiles are not an important issue even for people with sensitive, dry skin. However, theoretically, some irritant symptoms may appear for some people with very sensitive skin [Lahti, 1995].

Good performance of a zeolite based detergent depends on good formulation and correct use. The older zeolite formulations do not perform as well as the newer ones, where many of the earlier problems with zeolite have been solved [Hauthal, 1996].

## 4.3. Citrate

The Joint FAO/WHO Expert Committee on Food Additives has concluded that the acceptable daily intake for man of citrate is “not limited”, and the International Joint Commission of Canada and the United States concluded “the use of citrates in detergents poses no hazard to man” [Hoyt & Gewanter, 1992].

Sodium citrate has an $LD_{50}$ for mice of 7.1 g/kg, the signs of intoxication being acidosis and calcium deficiency. No mutagenicity or teratogenicity is reported or expected.

## 4.4. PCA

The toxicological behaviour of PCAs is generally not a concern according to Opgenorth [1992], and ECETOC [1993]. High molecular mass, slightly crosslinked polyacrylates are used as thickeners in cosmetics. Polyacrylic acid has not been associated with any adverse health effects including cancer risk. Teratogenicity and embryotoxicity tests with P(AA-MA) 70,000 proved negative as well.

# 5. Environmental aspects

Design considerations

Modern detergents using any of the three builder systems have been formulated to accommodate environmental concerns along with washing efficiency, i.e. they wash efficiently at low temperatures and the ingredients are non-ecotoxic after biological treatment. The surfactants constitute the group with the highest inherent ecotoxicity. Therefore, they have all been selected on the basis of their ready biodegradability. However, the long term effect on receiving ecosystems of biotreated effluents from washing machines using modern compact detergents has not been assessed as a whole, although extensive ecotoxicity and degradability testing of the individual constituents in the formulation have been conducted, [e.g. Schöberl, 1988; Schöberl & Bock, 1988].

## 5.1. Effluents

There are two main concerns with regard to the discharge of effluents containing used laundry detergents:

- Eutrophication.
- Adverse effects from xenobiotic substances in the detergents.

Biotreatment needed

As stated earlier, in almost all cases, effluents must pass an advanced biological wastewater treatment facility to become environmentally compatible. The concentration of phosphate in the final effluent is determined by the choice of treatment process applied, rather than by the concentration of phosphorus in the influent. Therefore, if STPP based detergents are used, advanced biological wastewater treatment in most cases needs to involve additional tertiary treatment. If the incoming concentration of phosphorus is high, large amounts of coagulants are needed, and the amount of sludge will increase, but the concentration in the final effluent can still be controlled by applying appropriate amounts of coagulants. Zeolite based detergents assist phosphorus control of the effluent [Siegrist & Boller, 1996].

There are situations, however, where efficient biotreatment is very difficult to achieve:

- During heavy rainfall, unless a separate storm water sewer is in use.
- During periods of frequent change between thaw and frost causing frequent snow melting.
- During longer periods of very strong frost.
- Under circumstances where investments in wastewater treatment facilities are generally insufficient.

Ranking of builders

If untreated wastewater is discharged, the zeolite/polycarboxylate detergents are probably the best choice, since they do not contribute to secondary eutrophication and have a high content of inert or slowly degradable materials. Surfactants, which are present in greater amounts in citrate/fatty acid than in STPP or zeolite/polycarboxylate based detergents, are known to be ecotoxic although easily biodegradable, so citrate/fatty acid detergents are less preferable in this situation. Secondary treatment will eliminate adverse effects from citrate/fatty acid detergents. STPP based detergents must be regarded the least environmentally compatible ones if discharged without tertiary treatment, due to the effect of secondary eutrophication.

If tertiary sewage treatment is used, all three detergent builder systems become equally compatible with regard to protection of the receiving waters.

### 5.1.1. Eutrophication

Eutrophication is usually defined as the various consequences of the enrichment of a water body by nutrients, particularly phosphorus and nitrogen. Wastewater discharge and agricultural land drainage are two anthropogenic processes that most frequently lead to eutrophication. Wastewater discharge is a point source, while nutrient losses from agriculture may originate from nutrient containing materials such as crop residues, manure, sewage sludge, other organic sources and mineral fertilizers, or erosion. Freshwater environments are normally limited on phosphorus, while marine environments are frequently nitrogen limited. Although a matter of dispute, this may be an oversimplification as some freshwater systems can be N-limited during the summer, some marine inlets may be P-limited during spring (after depletion of Si).

Initially, the discharge of inorganic phosphorus or nitrogen may lead to phytoplankton growth, which may serve as an increased food source for zooplancton, which also grow and thus increase the amount of food available to fish. Thus, initially, an increased fish stock may result from an enrichment of the habitat with nitrogen and phosphrorus, provided other micronutrients are also available and the environment is ecologically in balance. However, at a certain point, the algal growth may exceed the capacity of the ecosystem to convert it to secondary and higher production in the food chain, and the result becomes dense algal blooms, death and oxygen depletion caused by algal respiration (at night) and bacterial degradation of the organic matter (sedimented algal material).

The role of silica

The process of eutrophication is a complicated matter that does not depend on nitrogen and phosphorus alone, e.g. diatom algae are dependent on silicon [Egge et al., 1988]. Diatom phytoplankton populations are the preferred food for zooplankton and filtre feeders, and thus the basis of a large fish stock. Flagellates and bluegreen algae (cyanobacteria), on the other hand, are frequently poor food for most grazers. Therefore, favoured growth of flagellates and bluegreens more often leads to undesirable effects from eutrophication than diatom growth. Silicon insufficiency is considered a controlling factor in altering a diatom to a flagellate or bluegreen community [Officer & Ryther, 1980]. High sedimentation rates of chlorophyll biomass have been associated with silica deficiency in Chesapeake Bay [Conley & Malone, 1992]. Measurements from the coastal zones of the North Sea- and the River Elbe-influenced water masses show significant increases in nitrate and phosphorus in recent decades, while silicate has been constant or decreasing. Over the same period, the biomass of flagellates has increased by a factor of 6 to 16, while the biomass of diatoms has been constant or decreasing. Silica may be depleted after the algal spring bloom, and eutrophication problems are often related to summer blooming of phytoplankton [Scholten, 1996]. A concentration of silicate above 2 µM[8] is generally considered to favour diatom over flagellates [Egge & Aksnes, 1992].

### 5.1.2. Discharge of untreated domestic sewage

*TNO Report*

TNO in the Netherlands has published a report on the eutrophication effects of untreated domestic wastewater containing zeolite or phosphate based laundry detergents

[8] 1 M = 28 g Si/L (Si), 2 mM = 56 mg Si/L; 2 µM = 0.056 mg (Si)/L

[Scholten et al., 1994]. The report was supported by CEEP (Centre Européen d'Etudes de Polyphosphates), CEEP Spain and SCOPE (Scientific Committee on Phosphates in Europe). Their study illustrates the fact that eutrophication can be caused by increased nutrient loads, but also by suboptimal zooplankton and macrophyte dynamics leading to less efficient grazing. Therefore, there is not necessarily a linear relationship between phosphate loads and phytoplankton biomass. A healthy ecosystem would respond by increasing the zooplankton and thus the fish biomass, and in fact that has been demonstrated in some of the best Canadian salmon lakes in British Columbia, where indeed the salmon population increased after spraying the pure lakes with phosphate from aeroplanes. Only if the rate of algal biomass production exceeds the rate of algae removal does eutrophication occur, as was shown already in the 60s.

Scholten et al. [1994] used microcosm experiments to determine the eutrophication effects of untreated, artificially made (from urine and faeces) sewage mixed with phosphate based and zeolite based detergents. The phosphate based detergent was used for washing in concentrations of 3 g/L, while the zeolite based detergent required a larger dosage of 5.2 g/L according to the manufacturers. (This difference in dosage is not reflected any more in modern, compact STPP or zeolite based detergents [Hauthal, 1996; Test (Berlin), 1996; Test Achats (Belgium), 1996]). Three different microcosm set-ups were used—all of them fresh water systems.

The 'TNO experiment' was based on a very high nutrient Geestmerambacht water (tot-P = 1.6 ± 0.2 mg P/L; tot-N = 2.4 ± 0.1 mg/L and Si 6.3 ± 0.3 mg Si/L), which is totally unrealistic for Scandinavian lakes. The level of Si is so high that any "normal" eutrophication effect of phosphate due to a lack of silica as explained above is excluded, i.e. such a water could be predicted to be completely insensitive to additional phosphate loadings.

The 'Chambery microcosm study' was done at much lower nutrient levels (P = 0.01 mg/L and N = 0.45 mg/L), but no levels of silica were reported. This system was to a certain extent P-limited as the final P-concentration was lower than the initial one.

The 'Alicante microcosm studies' used water with reported contents of 5 – 30 µg P/L and is described as "relatively unpolluted".

*Findings*

The results from all three microcosm experiments were unanimous:

> The zeolite based detergent caused eutrophication at lower relative concentrations in the artificial sewage than the phosphate based detergent. This is due to the fact that larger dosages of zeolite based detergents were used to construct the artificial domestic water, according to the recommendations made by the manufacturers. In equal dosage no difference was observed.

It was concluded that the mechanism behind the adverse effect was the presence of surfactants in the washing water from the detergents, which led to intoxication of zooplankton and thus an increase in algal biomass.

*Our assessment*

The above conclusion is a technically correct interpretation of the results. However, the microcosms were insensitive to increasing phosphate exposure as:

- Initial levels of nutrients were high.
- In one experiment, the silicate level was also very high, which prevents unfavourable conditions for diatom algae and thus stimulates zooplankton growth. Silicate levels were not reported in the other two experimental set-ups.
- In an ecosystem having low levels of both N, P and Si, our prediction would be that the P-based detergent would be the one causing eutrophication sooner than the zeolite based one.
- The results only apply to the rather special case of discharge of untreated sewage. Biotreatment of the laundry water would have given a different result of the comparison of the two detergents, i.e. the surfactants would have been biodegraded/biotransformed and thus possibly non-ecotoxic. Therefore, the experiment remains inconclusive with regard to the true eutrofication effect of the two detergents, i.e. after biotreatment.
- The results are dependent on a higher dosage of the zeolite based detergent than the STPP based detergent. This was the case in earlier formulations, but not any more [Hauthal, 1996].

Zeolite is reported to be hydrolyzed to silica, sodium, and aluminium oxide with a half-time in sediment of ≈ 2 months [H.E. Allen et al., 1983], but highly dependent on pH and the complexed metal ion. This is probably too slow a rate of hydrolysis to make the Si in zeolite bioavailable.

Discharge of untreated washing water may cause the surfactants (and other sewage constituents, e.g. ammonia/ammonium ions) to express their ecotoxicity. However, passing a biological treatment plant or even the residence time in the sewer, for a couple of hours, would largely eliminate the ecotoxic potential of easily biodegradable surfactants, which are used in the formulation of both the phosphate based and the zeolite based detergents.

All in all the experimental design of the TNO study covers a very specialized case in which biotreated, artificial sewage mixed with untreated washing water from phosphate or zeolite based detergents is discharged (with zero residence time in a sewer) to freshwater ecosystems that have already very high levels of nutrients. The ecotoxicity caused by the surfactants under these circumstances cannot be generalised.

### 5.1.3. Xenobiotics

Most of the surfactants in a laundry detergent formulation are by nature xenobiotic compounds. Xenobiotic compounds that possess a combination of being slowly biodegradable and ecotoxic to aquatic life or slowly biodegradable and bioaccumulating are of most environmental concern. Table 4 presents environmental data on frequently used compounds in laundry detergents.

As can be seen from Table 4, the components of modern detergents are either non-ecotoxic/non-bioaccumulative or readily biodegradable. Thus, the main part of the COD – BOD of treated laundry effluents is made of polymers and other biological inert materials, with a possibility of some other minor components. Although polycarboxylates and phosphonates are not readily biodegradable, the are effectively removed in a biological wastewater treatment plant.

Today, detergents can be made exclusively from easily degradable or non-ecotoxic/non-bioaccumulative compounds, regardless of the preferred builder system. However, the formulation of individual detergents can vary quite a bit depending on the brand, and some formulations on the market are more environmentally compatible than others. The choice of builder system does not tell much about the environmental compatibility of a specific brand. All added compounds and the relative amounts of each compound will have to be taken into consideration.

**Table 4 Environmental properties of laundry detergent components.**

| Compound | Effect concentration EC50 / LC50 (mg/L) | | | Degradation | | Potentially bioaccumulative |
|---|---|---|---|---|---|---|
| | Algae | Crustacea | Fish | Aerobic | An-aerobic | log Po/w ≥ 3.0 |
| Surfactants | | | | | | |
| LAS | 0.5-120 | 0.1-30 | 0.4-23 | Yes | No | Yes[Å] |
| Alkylsulfates | 4-60 | 5-70 | 1.4-70 | Yes | Yes | Yes[Å] |
| Fatty acid soaps | 10-50 | - | 20-150 | Yes | Yes | Yes[Å] |
| Alcohol ethoxylates | 0.8-50 | 0.1-100 | 0.25-100 | Yes | Yes | Yes[Å] |
| Blockpolymers | - | >100 | >100 | No | No | Yes[Å] |
| Alkyl glycosides | 3.9-1500 | 12-550 | 2.5-550 | Yes | Yes | Yes[Å] |
| Builders | | | | | | |
| Zeolite A | 50-1000 | 380 | >500 | n.a.[Ç] | n.a.[Ç] | No |
| Polycarboxylates | >200 | >200 | >200 | No | No | No |
| NTA | 1-1000 | 100-1000 | 100-5500 | Yes | - | No |
| EDTA | 11 | 625-1030 | 150-2000 | No | No | No |
| Phosphonates | 0.4-40 | 300-500 | 150-8000 | No | No | - |
| Citrate | 80-640 | 80 | 625 | Yes | Yes | No |

[Å]Concentrates at the octanol/water interface.
[Ç]Not applicable
Source: [Miljøstyrelsen & Forbrugerstyrelsen, 1995].

## 5.2. Sludge handling

Advanced biological wastewater treatment is often perceived to involve some kind of activated sludge process. What this process does is to use energy to digest ≈50% of the organics and transfer the major part of the remaining pollutants from the aqueous phase to the solid phase, and society is left with a sludge problem. The builder systems do not add equally to the sludge problem: Zeolite/polycarboxylate ≥ STPP > Citrate/fatty acids in terms of the mass of sludge created. Citrate/fatty acids do add to the amount of biosludge, but much less than the two others, because ≈50 % of the carbon are lost in the metabolism.

Although there are many different sludge handling process that can be used, the three dominant ones in use being:

- Spreading on agricultural land.
- Incineration of the sludge—the ash goes to a land-fill.
- Landfilling of the sludge.

### 5.2.1. Agriculture

Although a great matter of dispute, there is no doubt that from an ecological point of view, the spreading of sludge on agricultural land is a sustainable technique, as it recycles waste materials back to nature. Particularly phosphate, which is spread in large quantities on agricultural land throughout Europe, is a valuable resource in this sludge. For this means of disposal to be environmentally compatible, the sludge should be:

- Low in concentrations of heavy metals, particularly Cd, Hg, Pb, Ni, Cu and Cr.
- Low in concentrations of persistent, xenobiotic compounds.
- High in concentrations of soil improvers such as calcium and magnesium and of fertilizers such as phosphorus.
- High in non-ecotoxic, organic material that improves the humus content of the soil.

If these conditions are met, then sludge application on land is by far the most environmentally compatible means of disposing sludge from municipal wastewater treatment.

STPP

Generally, phosphate in sludge is an advantage, when applied on agricultural land, because it can substitute commercial fertilizers. If sludge is applied correctly, the phosphate from STPP based detergents is directly recycled back to nature, and an equal amount of raw phosphate is saved on the resource side. If the sludge has a high phosphate content it may also be easier to get farmers to use the sludge on their land. However, phosphate in sludge can be bound as “organic” phosphate, biologically bound polyphosphate and as inorganic solids in chemically precipitated sludge. Phosphorus is well over 100 times more available to plants, when applied as mineral fertilizer or in sludge from biological phosphorus removal processes (organic phosphate or polyphosphate) as compared to sludge from alum of ferri chloride phosphorus removal processes [Kyle & McClintock, 1995]. It is possible that $Al^{3+}$ is more efficient in forming insoluble phosphate complexes than $Fe^{3+}$, if anoxic soil conditions in the field exist to reduce $Fe^{3+}$ to $Fe^{2+}$. Phosphate will then become re-dissolved in the agricultural field . However, this needs to be studied further [Kemira, 1996].

Therefore, if full advantage is to be taken of the phosphate in biosludge, biological phosphorus removal should be used together with moderate amounts of chemical coagulants, which should be ferri chloride rather than alum. Excessive amounts of free coagulants in the sludge in combination with a low soil pH could lead to the binding of phosphate coming e.g. from mineral fertilizers, thus increasing the need for fertilizer on the field [Madsen, 1996].

Zeolite

Zeolite is an inert material of little known value to farmland, but there are no harmful properties to it either. Ultimately, it will be hydrolysed to silica and aluminium oxide, which are also part of the natural minerals in soil.

Citrate

The organic content of the sludge is probably higher when citrate/fatty acid or zeolite builders are used. The soil improving properties of this fraction of the sludge is of no financial value to the farmers, but for society it is a cost efficient and environmentally compatible means of disposal.

Xenobiotics

The main concern is currently the level of heavy metals and xenobiotic compounds in the sludge. LAS is are of the the compounds that have been found in sludge from Danish sewage treatment plants [Kjølholt et al., 1995]. LAS is degraded aerobically in the soil if spread on farmland, but it may be needed in the future to compost the sludge prior to spreading on land in order to obtain sufficient degradation of LAS and to comply with proposed regulations.

PCAs are also found in sludge and can thus end up on farmland. They are much more slowly degradable than LAS, but they adsorb to solids so strongly that they are not transported into ground water, and they are generally non-ecotoxic as explained above [Opgenorth, 1992]. The chemical nature of PCAs makes it unlikely that they are taken up by crops, so spreading on farmland is not seen as a route to human exposure.

### 5.2.2. Incineration

Sludge that has too high levels of heavy metals is often incinerated[9], and the ash goes to a land fill. The highest contribution to ash from the three builders is zeolite > phosphate > citrate. Phosphate that has been incinerated is often so tightly bound to solids that it will not be taken up readily by plants. This was demonstrated in a recent study when straw was incinerated for its fuel value and the phosphate became so tightly bound in the ash that it had hardly any value as a P-fertilizer [I. Krüger Systems AS et al., 1992]. The environmental properties of the ash coming from incineration of sludge are not expected to be adversely changed due to a sludge content of compounds related to detergents.

[9] In Finland and Sweden incineration does not take place [Kemira, 1996].

### 5.2.3. Landfills

In some countries the capacity for incinerating sludge prior to land filling is too small, or it is politically not possible to incinerate the sludge due to fear of atmospheric contamination with e.g. dioxins. This dramatically increases the amount of sludge, which has to be sent to landfill, and again the order of contribution to sludge is the same zeolite ≥ phosphate > citrate. None of the compounds from detergents ending up in sludge are foreseen to cause any problems beside taking up capacity at the landfill. Availability of landfills is limited all over Europe right now, mostly due to the NIMBY (Not In My Back-Yard) principle.

# 6. LCA considerations

Life-cycle analyses (LCA) for zeolite and STPP based systems have been carried out [Morse et al., 1994; Wilson & Jones, 1994]. Although not being a full LCA study, a Delphi study involving 17 scientists from 8 European countries was directly focused on the Nordic countries [Wilson & Jones, 1995]. Neither of the above mentioned three studies included citrate/fatty acid, and all studies were based on the assumption that zeolite/polycarboxylate detergents required larger dosages than STPP based detergents. SCOPE, but not ZeoDet, was involved in these studies. Therefore, the studies had to rely on the original patents rather than actual information from the zeolite manufacturers [Hauthal, 1996].

ZeoDet has collaborated with the author of a new, peer reviewed life-cycle impact (LCI) study of zeolite. The study was performed along the newly published ISO/DIS 14040 guidelines and will be released this year [Hauthal, 1996]. In addition to the LCI data, this study contains an impact analysis of the switch from phosphate to zeolite containing detergents. Among the major findings is that zeolite based detergents do not need to contain a larger fraction of surfactants or necessarily require a larger dosage than STPP based detergents—it all depends on the individual formulation. This study was focused on zeolite detergents as it was felt that the previously conducted LCA studies lacked accurate information on these detergents.

The main conclusions from the studies in which SCOPE/Kemira collaborated [Morse et al., 1994; Wilson & Jones, 1994; Wilson & Jones, 1995] were that both phosphate and zeolite based detergents have small, negative or uncertain environmental impacts throughout their life-cycles, and that the pros and cons overall made them equally compatible. In the British study [Wilson & Jones, 1994], the penalty points for the STPP system was 107 and 110 points for the zeolite/poly-carboxylate system on an equivalent performance basis (higher dosage needed for zeolite based detergents). In the Nordic study the STPP system had only 95 points due to a more efficient P-removal from the wastewater. These points were for Sweden, and the authors estimate that similar results would have been obtained for Norway and Finland, while the situation for Denmark would reflect the British result more closely.

**Table 5. Comparison between detergent builders.**

| | STPP | Zeolite A/P | Citrate/fatty acids |
|---|---|---|---|
| Raw material | 2.34 kg rock phosphate needed per kg STPP produced. Needed for fertilizer. | Raw materials for zeolite include sand, bauxite and sodium chloride, all of which are plentiful. | Raw materials are essentially renewable biomass. |
| Waste products | Phosphogypsum from rock phosphate processing. Calcium sulphate from calcination. | Red mud from aluminum oxide. | Waste products from fermentation. The environmental compatibility depends on the utilization of waste product. |
| Water | ≈60 $m^3$/t STPP of wastewater ≈130 $m^3$/t STPP of cooling water. | ≈7 $m^3$/t zeolite of wastewater ≈44 $m^3$/t zeolite of cooling water. | Larger wastewater production expected than from STPP. Production takes place in China. |
| Washing efficiency | Electron microscopy examinations have revealed that STPP based detergents provide the cleanest wash. To what extent the superiority is achieved by overdosing of zeolite detergents is not clear. | Independent tests of new zeolite based detergents have shown excellent performance at a similar surfactant and dosage level as STPP based detergents. | To achieve the same washing efficiency, 500% more anionic surfactants are needed. These are essentially removed at 100% from the effluent, but a fraction is expected to end up in the sludge. Composting of sludge should degrade these surfactants. |
| Overall builder system | STPP provide an excellent builder system for laundry detergents. | By adding co-builders such as polycarboxylates (Zeolite A only) and by optimization of the surfactant system, zeolite-containing laundry detergents become comparable to phosphate-based detergents | Citrate/fatty acids based builder systems are able to perform as well as STPP based detergents, but at a higher cost. |
| Sewage treatment plants | P is an essential nutrient for biological processes. However, in most instances there is sufficient P in the raw sewage to meet the need. Proven technologies exist to control the effluent P concentration independently of the influent concentration. | It has been speculated that zeolite based detergents are involved in the declined sludge quality and in operational problems at Swedish municipal sewage treatment plants during the last five years. There are no hard facts to support this speculation. | Citrate is easily degraded. Fatty acids are aerobically degradable. There should be no effects on treatment plants, unless fatty acids for some reason are specific substrates for filamentous bacteria. |
| Biological nutrient removal | Increasing amounts of phosphorus in the influent necessitate the adding of coagulants such as ferri chloride or alum. | There is evidence that zeolite detergents assist the precipitation of biosludge and thus increases sludge age and consequently nitrification, which is the rate determining step of biological nutrient removal. | Citrate is a very efficient source of carbon for biological phosphorus removal and denitrification, so it will improve the performance of most treatment plants. |

| | STPP | Zeolite A/P | Citrate/fatty acids |
|---|---|---|---|
| Sludge | P is phytoavailable, if bound in an organic matrix or biological phosphorus removal is used. Not immediately phytoavailable if alum or iron has been used to precipitate sludge. P from sludge is not in need on most fields where manure from animals is spread. | Increases sludge loads 10-15% on mass. Sludge properties improved. | Sludge loads from citrate/fatty acids are expected to be smaller than from any of the other two builder systems. |
| Eutrophication | Discharge of P plays an important role in eutrophication. However, the elimination of P alone has never restored a fresh water system destroyed after eutrofication. Biological sewage treatment with nutrient removal minimises the problem. | Zeolites have very little effect of eutrophication. Zeolites can be hydrolysed (but slowly) to provide silica for diatom algae, and if these algae dominate the microfauna, eutrophication becomes less of a problem, because they are good food items for zooplankton. | Discharge of untreated citrate/fatty acids will add to eutrofication and immediate oxygen depletion can be a problem. However, long term effects should be less than for STPP based detergents. After simple biotreatment there should be no effects. |
| Ecotoxicity | Phosphate is essentially non-ecotoxic. It is a vital compound for living organisms. | Zeolite A/P are essentially inert to living organisms. | No problem for citrate. Fatty acids can be ecotoxic to fish. |

Life-cycle assessments are very complicated, and the original LCA studies [Morse et al., 1994; Wilson & Jones, 1994; Wilson & Jones, 1995] may need to be revised in order to follow the new ISO/DIS 14040 LCA guidelines. The assumptions made prior to an LCA analysis are in most cases determining for the outcome of the analysis, i.e. depending on the presumptions virtually anything can be proven. Therefore, LCA studies are seldom useful for political decision making, but they can be a good tool for a company that honestly wants to assess the pros and cons of a particular product. Many LCA studies have been conducted solely for the purpose of confirming a decision that was already taken. In the case of detergent builders, the LCA is indeed very complicated, and there are so many local factors involved that LCA will not provide a universal answer as to which builder system is the environmentally most compatible one. Factors such as hardness of water, sewage treatment practice, laundry habits etc. are so variable that each of the detergent builders will turn out to be the preferable one under any specific set of circumstances. Table 5 provides a review of some of the important factors discussed in the previous chapters, but no general recommendation for a particular builder can be made. The specific local condition will have to be evaluated.

# 7. Conclusions

All three builder systems have their pros and cons with regard to the aspects discussed in this report.

The content of surfactants in detergents using different builder systems is roughly the same in the case of non-ionic surfactants, but varies greatly when it comes to anionic surfactants. The relative amount of anionic surfactants in zeolite and phosphate detergent systems is of roughly similar size. In liquid detergents the builder system is made of fatty acids and larger amounts of anionic surfactants are used. In phosphate based detergents, sodium sulphate is added to improve the solubility and efficiency of surfactants.

From a health perspective, the three builder systems are all safe in use. Zeolite-based detergents may leave more residues in cloth, particularly after using badly formulated or produced brands or after overdosing.

STPP based detergents may be superior to the others in terms of pure washing efficiency. However, much research has been put into developing zeolite/polycarboxylate and citrate/fatty acid builder systems, so STPP based detergents do not any more have a significantly better performance compared to the other builder systems.

Citrate is superior to the others in terms of wastewater treatment, because it is an excellent substrate for biological phosphorus removal and denitrification. However, modern wastewater treatment plants can handle extra amounts of phosphate as well as zeolite—but at a cost of increased sludge handling.

The role of fatty acids and surfactants in the recent problems of foaming and less efficient oxygen transfer in aerators needs to be studied in more detail. They are not directly linked to the choice of builder systems, except maybe for the citrate/fatty acid builder system (but this contribution is small compared to the background).

During cold periods when a sewage treatment plant is not working efficiently, zeolite provides the better builder system, because it does not add so much to the eutrophication as phosphate or to oxygen depletion as citrate does. STPP based detergents should not be used, if the wastewater treatment plant in the area does not remove phosphorus. Thus, when untreated sewage is discharged, the relative role of detergent builders in adding to a eutrophication problem is STPP > citrate/fatty acids > zeolite/polycarboxylate.

With proper formulations, i.e. the choice of surfactants and other substances in the detergent, all three builders can be part of environmentally compatible products. However, good sewage treatment, including biological phosphorus removal and denitrification as well as extended sludge treatment prior to spreading on agricultural land, is a prerequisite for environmentally compatible laundry detergents. Correct dosage—taking into account the hardness of the local water, correct washing temperatures—not too high, but generally not below 40 °C, and good rinsing after wash are other prerequisites.

# 8. References


Alder, A., W. Giger & C. Schaffner, 1996. "Phosphatatsstoffe in Wasch- und Reinigungsmitteln: Beelzububen oder akzeptierbare Chemikalien?". Zusammenfassung der Referate: *Das Janusgesicht des Phosphors, EAWAG-Infotag 10. September 1996,* Dübendorff, Schweiz.

Allen, H.E., S.H. Cho & T.A. Neubecker, 1983. "Ion Exchange and Hydrolysis of Type A Zeolite in Natural Waters". *Water Res.* **17**(12): 1871-1879.

Andresen, H.-J., 1996. *Colgate-Palmolive AS*, Smedeland 9, Glostrup, DK-2600, Personal Communication.

Anonymous, 1994. "Inspection of Municipal Treatment Plants 1993" ((in Danish)). written by *Teknisk Forvaltning, Miljøafdelingen*, *Frederiksborg Amt*, Hillerød, Denmark.

Böhnke, B., M. Defrain, E. Dorgeloh & T. Grünebaum, 1992. "Cost Evaluation of Detergent Constituents for Municipal Sewage Treatment Plants" ((in German)). *SÖFW-Journal* **118**(8):

Chambon, P., 1992. "Criteria Used for Measuring Environmental Impacts of Detergents. Environmental Impact Studies of Compact and Conventional Detergents". *SCOPE International Media Forum,* 28 February, Copenhagen.

Christophliemk, P., P. Gerike & M. Potokar, 1992. "Zeolites". *In:* Detergents, N.T.d. Oude (ed.), Vol. Vol. 3, Part F: Anthopogenic Compounds, Book Series: The Handbook of Environmental Chemistry, O. Hutzinger (ed.). *Springer-Verlag*, Berlin, Heidelberg, p. 205-228.

Conley, D.J. & T.C. Malone, 1992. "Annual Cycle of Dissolved Silicate in Chesapeake Bay: Implications for the Production and Fate of Phytoplancton Biomass". *Mar. Ecol. Prog. Ser.* **81**: 121-128.

Constant, J., 1992. "Methods for Testing Detergent Washing Efficiency". *SCOPE International Media Forum,* 28 February, Copenhagen.

Crosfield, 1996. “Doucil A24. The New P-Type Zeolite for Detergent Applications”. *Crosfield BV*, Eijsden, The Netherlands.

ECE, 1980. “Substitutes for Tripolyphosphate in Detergents”. ECE/CHEM/80, United Nations *Economic Commission for Europe*.

ECETOC, November, 1993. “Polycarboxylates Polymers as Used in Detergents”. Joint Assessment of Commodity Chemicals No. 23. *ECETOC*, Brussels, Belgium.

Egge, J.K. & D. Aksnes, 1992. “Silicate as regulating nutrient in phytoplankton competition”. *Mar. Ecol. Prog. Ser.* **83**: 281-289.

Egge, J.K., D.L. Aksnes & B.R. Heimdal, 1988. “Silikatets rolle i marine algeoppblomstringer” (In Swedish)). *Naturen* **1988**(5): 187-189.

Farm, C., 1994. “Flytande tvättmedel sämre och dyrare”. *Råd & Rön* **94**(11): 3p.

Feijtel, T.C.J. & E.J. van de Plassche, 1995. “Environmental Risk Characterization of 4 Major Surfactants Used in the Netherlands”. Report No. 679101 025, *Dutch Soap Association & National Institute of Public Health and the Environment*, Bilthoven, The Netherlands.

Folke, J., 1995. “Environmental Aspects of Compact Liquid Detergents—Comments on the "Stockholm Vatten" Investigation”. Note, November 1995, written by *European Environmental Research Group Ltd*, Gilleleje, Denmark, for *Procter & Gamble, Scandinavia,*, Stockholm, Sweden. Contact Ms. M. Nygren, fax +46 8 477 8410.

Frostell, B., Bengt, Hultman, J. Röttorp & P. Solyom, 1995. “Nya kemikalier—En utmaning för kommunala reningsverk” (in Swedish). Förstudie. Rapport nr. 1995-13, *Svenska Vatten- och Avloppsverksföreningen, VAV*, Stockholm.

Gleisberg, D., 1992. “Phosphate”. *In:* Detergents, N.T.d. Oude (ed.), Vol. Vol. 3, Part F: Anthopogenic Compounds, Book Series: The Handbook of Environmental Chemistry, O. Hutzinger (ed.). *Springer-Verlag*, Berlin, Heidelberg, p. 179-203.

Gregory, G.I., 1992. “Global Structure of the Phosphate Fertilizer Industry”. Proceedings of an international workshop: *“Phosphate Fertilizers and The Environment”,* Tampa, Florida, USA, March 23-27 1992, *IFDC (International Fertilizer Development Center),* Muscle Shoals, Alabama, USA.

Hasling, A.B., O. Dalgaard, M.M. Sørensen & D.E. Thornberg, 1990. "Economics of Treatment of Industrial Effluents in Municipal Treatment Systems". (In Danish), Spildevandsforskning fra Miljøstyrelsen nr. 15. *Danish National Environmental Protection Agency, Ministry of Environment*.

Hauthal, H.G., 1996. "Laundry Detergent Zeolites in an Ecobalance Spotlight". *SÖFW-Journal* **13**: (in press).

Hoyt, H.L. & H.L. Gewanter, 1992. "Citrate". *In:* Detergents, N.T.d. Oude (ed.), Vol. Vol. 3, Part F: Anthopogenic Compounds, Book Series: The Handbook of Environmental Chemistry, O. Hutzinger (ed.). *Springer-Verlag*, Berlin, Heidelberg, p. 229-242.

I. Krüger Systems AS, Statens Planteavlsforsøg; Askov Forsøgsstation, Kemira Danmark A/S & Landbocenteret; Brønderslev, 1992. "Slam og halmaske til gødning". Spildevandsforskning fra Miljøstyrelsen nr. 28. *Miljøstyrelsen*, København, Danmark.

IKW, 1996. "Waschmittel-Verbrauch". (Photocopy from a report). Frankfurt.

Johnston, E., 1992. "Domestic Laundering, the Consumer and the Environment". *SCOPE International Media Forum,* 28 February, Copenhagen.

Kaarina Kuusimaa, 1995. "Inadequate rinsing of silicate particles in detergents". (in Finnish).

Kemikalieinspektionen, 1994. "Tvätt- Disk och Rengöringsmedel - redovisning av ett regeringsuppdrag", p 56.

Kemira, 1994. "Vad innebär ren tvätt". *Fact Sheet from Kemira Kemi AB* .

Kemira, 1996. "Comments Made to Draft Report". Association of Detergent Zeolite Producers, *Kemira Kemi AB*, Helsingborg, Sweden.

Kirk-Othmer, 1985. "Citric Adic". *In:* Concise Encyclopedia of Chemical Technology. *Jonh Wiley & Sons*, p. 281-282.

Kjølholt, J., H.V. Andersen & C. Poll, 1995. "Forekomst og effekter af miljøfremmede stoffer i spildevandsslam" (In

Danish). Arbejdsrapport nr. 15. *Miljøstyrelsen*, København, Danmark.

Konsumentverket, 1996. "Information Given at a Seminar Held at KTF Regarding Emerging Problems With Fabric Washing and Possibly Also Washing Machines". Personal Communication, 14 February.

Kuluttaja (The Consumer), 1995. (In Finnish). No. 4/93.

Kyle, M.A. & S.A. McClintock, 1995. "The Availability of Phosphorus in Municipal Wastewater Sludge as a Function of the Phosphorus Removal Process and Sludge Treatment Method". *Water Environment Research* **67**(3): 282-290.

Lahti, A., 1995. *Department of Dermatology*, University of Oulu, Finland, Personal Communication.

Leal, S., 1992. "Comparative Washing Efficiency and Environmental Impacts Tests of Compact and Conventional Detergents". *SCOPE International Media Forum,* 28 February, Copenhagen.

Madsen, C., 1996. "Sludge Application on Farm Land in Denmark". *Nordsjællands Landboforening*, Hillerød, Denmark, Personal Communication.

Matthies, V.W., A. Löhr & H. Ippen, 1990. "Bedeutung von Rückständen von Textilwaschmitteln aus dermatotoxikologischer Sicht" (in German). *Dermatosen* **38**(6): 184-189.

Miljøstyrelsen & Forbrugerstyrelsen, 1995. "Fakta om miljø – Vaske og rengøringsmidler" (in Danish). ISBN 87-7408-5093, *Forbrugerstyrelsen*, København, Denmark.

MoE Bonn, 1992. "Comments on the Use of Phosphate-free Detergents". March 1992, *Information by the Federal Minister for the Environment, Nature Conservation and Reactor Safety*, Bonn, Germany.

Morse, G.K., J.N. Lester & R. Perry, 1994. "The Environmental and Economic Impact of Key Detergent Builder Systems in the European Union". ISBN 0 948411 090, written by *Environmental Engineering Laboratory, Imperial College of Science, Technology and Medicine*, London SW7 2BU, © *Centre Européen d'Études des Polyphosphates E.V.*, Brussels, Belgium.

Müller, E., 1996. "Phosphatverbot für Washmittel – Ein Beispiel für Massnahmen an der Quelle". Zusammenfassung der

Referate: *Das Janusgesicht des Phosphors, EAWAG-Infotag 10. September 1996,* Dübendorff, Schweiz.

Naturvårdsverket Informerar, 1992. "Rena Fakta", p. 13.

Officer, C.B. & J.H. Ryther, 1980. "The Possible Importance of Silicon in Marine Eutrophication". *Mar. Ecol. Prog. Ser.* **3**: 83-91.

Opgenorth, H.-J., 1992. "Polymeric Materials Polycarboxylates". *In:* Detergents, N.T.d. Oude (ed.), Vol. Vol. 3, Part F: Anthopogenic Compounds, Book Series: The Handbook of Environmental Chemistry, O. Hutzinger (ed.). *Springer-Verlag*, Berlin, Heidelberg, p. 337-350.

P&G, 1994. *Weekly Monitoring Report,* Finland - Media, No. 10, 1994-02-24.

Schöberl, P., March/April, 1988. "Ecological Relevant Data for Non-Tensides in Washing and Cleaning Agents" ((In German)). Reports on H.A.-Detergents. Sonderdruck 5263 Erschienen in Tenside Detergents, pp 86-107, written by *Marl und L. Huber, München*, *Sachstandsbericht*, Germany.

Schöberl, P. & K.J. Bock, March/April, 1988. "Ecological Relevant Data for Tensides in Washing and Cleaning Agents" ((In German)). Reports on H.A.-Detergents. Sonderdruck 5263 Erschienen in Tenside Detergents, pp 86-107, written by *Marl und L. Huber, München*, *Sachstandsbericht*, Germany.

Scholten, M.C.T., 1996. "Comments Made to Draft Report". *TNO Environmental Sciences*, Delft, The Netherlands.

Scholten, M.C.T., R.G. Jak & E.M. Foekema, 1994. "Ecological Control of Algal Densities". TNO-MW-R94/280, written by *TNO Environmental Sciences*, Den Helder, and published by *TNO*, Delft, The Netherlands.

Schowanek, D., 1996. *P&G European Technical Centre*, Strombeek-Bever, Belgium, Personal Communication.

SCOPE, 1992. "Disagreement over Scandinavian Green Label for Detergents". *Press release* 1992-02-26.

Siegrist, H. & M. Boller, 1996. "Auswirkungen des Phosphatvebots auf die Abwasserreinigung" (Including personnal information). *Das Janusgesicht des Phosphors, EAWAG-Infotag 10. September 1996,* Dübendorff, Schweiz.

SIS Miljömärkning, 1996. "Information Given at a Seminar Regarding Emerging Operating Problems at Swedish Sewage

Treatment Plants". *KVL*, Stockholm, Sweden, Personal Communication, 24 January.

Smulders, E. & P. Krings, 1990. "Detergents for the 1990s". *Chemistry & Industry*(19 March): 160-163.

SYSAV, 1992. "Slamspridning på åkermark". Results from 10 years field trials in south-west Skåne, written by *Malmöhus Läns Hushållningssällskap & VA-teknik*, Bjärred & Lunds Tekniska Högskola, *SYSAV Utveckling AB*, Malmö.

Test (Berlin), 1995. "Sauber oder sparsam". *Test* **95**(10): 69-75.

Test (Berlin), 1996. "Wäsche und Wasser sauber?". *Test* **96**(7): 65-69.

Test Achats (Belgium), 1996. "Les poudres à lessiver classiques". *Test Achats* **1996**(March): 4 pages.

Ullmann, 4th ed. "Aluminiumoxid". *In:* Ullmanns Encyklopädie der technischen Chemie, (4., neubearbeitete und erweiterte Auflage Ed.), Vol. 7. *Verlag Chemie*, Weinheim/Bergstr., p. 305-323.

Ullmann, 5th ed. "Aluminum Oxide". *In:* Ullmanns Encyclopedia of Industrial Chemistry, (Fifth, Completely Revised Edition Ed.), Vol. A1. *VCH*, USA, p. 581-582.

Upadek, H., B. Kottwitz & B. Schreck, 1996. "Zeolites and New Silicates as Detergent Raw Materials". *8. Deutsche Zeolith-Tagung,* 3.-4. März, *Berlin-Adlershof,* Berlin, Federal Republic of Germany, p. PL3.

Upadek, H. & P. Krings, 1991. "Detergent Trends with Regard to Performance and Environmental Compatibility". *30th International Man-Made Fibres Congress,* 12-14 June, Dornbirn/Austria.

Upadek, H., P. Krings & E.J. Smulders, 1990. "Zeolite A and Co-builders in Non-phosphate Detergents". *Chemicaoggi*(Jan.-Feb.): 61-67.

Valdmaa, K., 1986. "Long-Term Field Trials with Wastewater Sludge in Comparison to Farmyard Manure and Commercial Fertilizer". Proceedings from the 2nd International Gothenburg Symposium: *Recycling in Chemical Water and Wastewater Treatment,* Berlin, Germany, *Institut für Siedlungswasserwirtschaft,* Karlsruhe, p. 271-282.

van Kauwenberg, S.J., 1992. "The Global Phosphate Rock Resource Base—Technical and Economic Considerations".

Proceedings of an international workshop: *Phosphate fertilizers and the environment,* Tampa, Florida, USA, March 23-27 1992, *IFDC (International Fertilizer Development Center),* Muscle Shoals, Alabama, USA.

Wahlberg, C., 1995. "Detergents—Effects on Wastewater Treatment Plants and Environment" (in Swedish). (Tvättmedel—Effekter på reningsverk och miljö). Report No. 1995-09, written by *Stockholm Vatten*, Stockholm, Sweden, and published by *Svenska vatten- och avloppsföreningen VAV*, Stockholm.

Wilson, B. & B. Jones, 1994. "The Phosphate Report—A Life Cycle Study to Evaluate the Environmental Impact of Phosphates and Zeolite A-PCA as Alternative Builders in UK Laundry Detergent Formulations". Report, written by *Landbank Environmental Research & Consulting*, by a sponsorship from *Albright & Wilson Ltd.*, London, UK.

Wilson, B. & B. Jones, 1995. "The Swedish Phosphate Report—A Delphi Study to Compare the Environmental Impact of Detergent Builders in Nordic Countries and the Implication for Sustainable Management of Freshwater Resources in Europe". Report, written by *Landbank Environmental Research & Consulting*, by a sponsorship from *Kemira AB*, Helsingborg, Sweden.

Zehnder, A.J.B., 1996. "Blick über die Grenzen". Zusammenfassung der Referate: *Das Janusgesicht des Phosphors, EAWAG-Infotag 10. September 1996,* Dübendorff, Schweiz.

ZeoDet, 1994. "The Use of Zeolite in Detergents". Association of Detergent Zeolite Producers, *CEFIC*, Brussels, Belgium.

ZeoDet, 1996. "Comments made to draft report". Association of Detergent Zeolite Producers, *CEFIC*, Brussels, Belgium.

Ødegaard, H., 1995. "An Evaluation of Cost Efficiency and Sustainability of Different Wastewater Treatment Processes". *Vatten* **51**(4): 291-299.